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On bultfonteinite, a new fluorine-bearing hydrous calcium silicate from South Africa.

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THIS new mineral was first found by a miner named Cann in 1903 or 1904 on the 480-foot level of the Bultfontein mine at Kimberley. It occurred, associated with calcite, apophyllite, and natrolite, in a large 'horse' of dolerite and shale fragments enclosed in kimberlite. This huge inclusion, several hundred feet in height, undoubtedly formed part of the country-rock that now encloses the kimberlite pipe. The specimens of the new mineral were considered to be natrolite and were presented to Mr. A. F. Williams. Several years later the same mineral was found by Mr. C. E. Adams in the Dutoitspan mine, which is located about half a mile from the Bultfontein mine; he presented his specimens to the MacGregor Museum at Kimberley. Recently, Mr. Miller, Underground Manager of the Jagersfontein mine in Orange River Colony, discovered the new mineral in that mine, which is located 100 miles south-east of Kimberley.

[1] Mr. John Parry, Chief Chemist of the De Beers Consolidated Mines at Kimberley, died on October 6, 1931.

After the description of the new mineral afwillite[1] had been published, Mr. Williams realized that the specimens of bultfonteinite in his collection were different from natrolite and probably represented a new mineral. Accordingly, at his request, the material was investigated chemically by Mr. Parry, Chemist of the De Beers Consolidated Mines, and found to be unlike any mineral heretofore described. Likewise its crystallographical and optical properties, determined by Mr. Wright at Mr. Williams's request, proved that it is a new mineral of interesting properties.

The determinative work on this mineral has not been an easy matter and the results obtained are not of the highest accuracy because of its relatively poor crystallographical development, its intricate polysynthetic twinning phenomena, and its peculiar chemical composition. In this connexion it may be stated that without the use of the Fedorov universal stage the optical measurements which have been obtained would hardly have been possible.

The significant chemical feature of bultfonteinite is the presence of fluorine and its resemblance in chemical aspects to the mineral afwillite. The chemical analysis and tests were made chiefly on material from the Bultfontein mine. Part of a large pink radial spherulite measuring an inch and a half in diameter served for the several tests and determinations. This is the only radial spherulite of large size that has thus far been discovered. The remaining few specimens of the mineral are small radial spherulites, either attached to larger calcite crystals or to the country-rock matrix. Calcite and bultfonteinite were deposited in part simultaneously; however, the formation of bultfonteinite continued after that of calcite. Somewhat later small crystals of a second new mineral, a hydrous calcium sulphate, still to be described, were deposited. Individual crystals of bultfonteinite project out as radial extensions from small spherulites.

The methods followed in the chemical analysis were standard. In addition to the analysis a number of special tests were performed to ascertain the exact nature of the substance and its relation to afwillite.

From this analysis the formula $2Ca(OH,F)_2.SiO_2$ can be deduced, although the agreement is not close, especially with reference to the silica and lime. A more exact agreement is given by the formula $11Ca(OH,F)_2.5SiO_2$. The analyses computed from these formulas

[1] J. Parry and F. E. Wright, Min. Mag., 1925, vol. 20, p. 277.

are listed in columns 4 and 5 of table 1. In both cases the alumina and ferric iron oxide are included with the lime. The material was carefully selected for the chemical analysis; examination of the large pink spherulite failed to reveal the presence of substances other than bultfonteinite.

TABLE 1. *Chemical analysis of bultfonteinite.* (Analyst, John Parry.)

	Per cent.	Molecular ratios.	$2Ca(OH,F)_2.SiO_2$.	$11Ca(OH,F)_2.5SiO_2$.
SiO_2	26·50	0·4412	28·58	26·68
Al_2O_3, Fe_2O_3	0·72	0·0055	—	—
CaO	54·20	0·9666	53·37	54·79
H_2O	13·36	0·7414	13·06	13·40
F	8·81	0·4637	8·63	8·87
	103·59		103·64	103·74
Less O	3·71		3·64	3·74
	99·88		100·00	100·00

The following chemical behaviour characterizes bultfonteinite. The powder rubbed down with a little water and then filtered yields a solution showing strong alkaline reaction with litmus and phenolphthalein. The alkali in solution was found to be calcium hydroxide and that only. The fine powder moistened first with water and then mixed with dilute hydrochloric acid and shaken vigorously produces a firm clear jelly. On treating the powder with strong acids great heat is at once generated. When 0·1 gram of the substance is treated with water and then with 10 c.c. of half-normal hydrochloric acid a clear solution is obtained almost at once. When a definite amount of powdered bultfonteinite is shaken with a measured quantity of pure water and titrated at convenient intervals with standard acid, it is found that calcium hydroxide is being continuously dissolved, until, after a prolonged contact of several days, a total limiting amount of 41·2 % lime (CaO) is taken up. When a definite quantity of bultfonteinite powder is dissolved in a measured quantity of standard acid and the unused acid is determined, it is found that the amount of lime thus taken up is 41·2 %. When, however, the bultfonteinite powder is first strongly heated over a blast-lamp and then placed in prolonged contact with pure water, measurements show that the total limiting quantity of lime taken up is 16·8 % lime (CaO).

These reactions are easily understood if the formula is written $2Ca(OH)_2.2SiO_2 + CaF_2.Ca(OH)_2$. The total amount of lime entering

into solution on prolonged contact with water is then represented by $Ca(OH)_2$ in the second part of the formula. On heating to a high temperature calcium metasilicate is formed; only the free CaO not combined with silica or fluorine is then reacted upon by water. Expressed in these terms the analysis reads:

TABLE 2. *Recast of analysis of bultfonteinite.*

	1.	1*a*.	2.	2*a*.
SiO_2	26·50	26·53	26·50	26·64
Al_2O_3, Fe_2O_3	0·72	0·72	—	—
CaO*	24·74	24·77	24·74	24·87
CaO†	16·46	16·48	16·77	16·86
CaF_2	18·10	18·12	18·10	18·20
H_2O	13·36	13·38	13·36	13·43
	99·88	100·00	99·47	100·00

* Portion of lime which on heating combines with silica to form calcium metasilicate.

† Excess of free lime over and above that needed to form calcium metasilicate.

In column 1 the alumina and iron oxide are listed; but in column 2 they are combined with the lime and are treated as entering with the lime into the silicate. In column 1 the total free lime available for solution in water is 41·2 %. On heating to a high temperature calcium metasilicate is formed and only the excess lime, or 16·5 %, is available to enter into solution according to column 1; 16·8 % according to column 2. In columns 1 *a* and 2*a* the percentages are adjusted to 100 %.

Chemical similarities with afwillite.—The mineral afwillite occurs under conditions quite similar to those obtaining for bultfonteinite. The composition of afwillite may be written $3CaO.2SiO_2.3H_2O$ or $2H_2CaSiO_4.Ca(OH)_2$. Like bultfonteinite, afwillite powder, when shaken with pure water and titrated with standard acid, loses lime continuously, until after 36 hours nearly the whole of the lime has gone into solution. On heating over a blast-lamp, however, only 23·17 % lime is dissolved even after 72 hours' contact with water. This quantity represents the lime which, on heat treatment, is in excess of the amount needed to form the metasilicate. Afwillite is completely soluble in acid; the amount of acid used in this operation is exactly equivalent to the lime required for the complete afwillite molecule.

It is possible to express the composition of bultfonteinite in terms of afwillite plus fluorite and calcium hydroxide, thus :

$3CaO.2SiO_2.3H_2O$	75·53 %
Al_2O_3 }	0·72
Fe_2O_3 }	
CaF_2	18·10
$Ca(OH)_2$	5·40
	99·75

The question arises : Does bultfonteinite represent possibly a product formed as the result of the attack of a fluorine- or hydrofluoric acid-bearing solution on afwillite ? The amount of calcium hydroxide equivalent to 18·10 % CaF_2 is 17·17 ; this amount added to the 5·40 calcium hydroxide already present yields 22·57. In afwillite the free $Ca(OH)_2$ amounts to 21·64 % as computed, or 23·1 % as determined. This agreement is quite remarkable, and suggests that possibly the afwillite molecule was attacked, its silicate of lime removed, and its calcium hydroxide partially disintegrated by fluorine.

On heating in a blowpipe or gas flame, fragments of bultfonteinite become dull white and porcelain-like. No decrepitation or traces of melting were observed ; the fragments glow intensely at higher temperatures and show the calcium flame reaction. Examined under a microscope the white material obtained on heating was turbid and evidently decomposed.

When powdered bultfonteinite is heated in a dry test-tube, water is given off freely and condenses at the cold end of the tube. A series of heating experiments was made at the Geophysical Laboratory to ascertain the amount of water liberated at different temperatures. The powdered material was heated in a platinum crucible in an electric resistance furnace ; temperatures were read with the aid of a platinum, and platinum + 10 % rhodium, thermo-element and a millivoltmeter. Two different runs were made on two different samples. The results are listed in table 3.

The agreement between these runs is only fairly good ; the escape of the water at the different temperatures is remarkably slow, and very long exposures at a given temperature are required if equilibrium is to be attained ; many of the exposures in these runs were not of sufficient duration to insure equilibrium. The results do show, however, that the water given off is all of the same kind and is water of constitution and not water of crystallization as in the zeolites.

The greater part of the water escapes between 250° and 350° C. The mineral afwillite behaves in the same manner on heating and loses its water gradually, but more rapidly at 300° than at any other temperature.

TABLE 3. *Loss of water by bultfonteinite at different temperatures.*

Temperature in degrees C.	Time in hours of exposure at the given temperature.	Cumulative total percentage loss in weight.
First run, Nov. 9 to 12, 1931. Weight of sample 0·4208 gram.		
250°	1·25	0·60
250–255°	16·67	1·90
350	2·17	4·42
350	2·50	9·10
350	17·50	12·50
350	4·00	12·50
600	2·00	12·98
600	16·75	12·98
900	3·50	13·17
1000	2·00	13·28
Second run, Nov. 20 to 25, 1931. Weight of sample 0·8130 gram.		
110°	2·00	0·09
300–310°	19·67	3·49
270–300	23·30	3·63
500	3·00	12·99
500	19·67	12·99
700	29·75	13·05
870–900	16·25	13·52
1000	6·25	14·13

Blowpipe tests.—Heated in a closed tube, fragments of the mineral lose water which gathers in the restricted neck of the tube; at the same time they become white and porcelain-like. Before the blowpipe the needles glow intensely with the characteristic brilliance of lime-bearing minerals and become white and enamel-like; but they do not melt; even sharp edges show little evidence of rounding.

Specific gravity.—The specific gravity of bultfonteinite was found by immersion in pure benzene (C_6H_6), which has no solvent action on it, to be 2·73.

Crystallographical properties.—In the specimens thus far collected, bultfonteinite occurs in the form of small radial spherulites and groups of small radiating acicular crystals measuring from 0·5 to 2 mm. in length. Many of the minute crystals are colourless and water-clear. In masses, especially in the single large radial spherulite, the colour is pale pink. The prismatic crystals are well

TABLE 4. *Crystal angles of bultfonteinite.* (*Triclinic.*)

$p_0 = 1{\cdot}0145$ $\lambda = 85° 41'$ $a = 0{\cdot}6756$ $\alpha = 94° 17'$ $x_0 = 0{\cdot}0345$ $d = 0{\cdot}0828$
$q_0 = 0{\cdot}6869$ $\mu = 87° 57'$ $b = 1$ $\beta = 91° 59'$ $y_0 = 0{\cdot}0753$ $\delta = 24° 37'$
$r_0 = 1$ $\nu = 89° 07'$ $c = 0{\cdot}6873$ $\gamma = 90° 44'$ $h = 0{\cdot}9966$

No.	Letter.	Symbol Gdt.	Miller.	ϕ.	ρ.	ξ_0.	η_0.	ξ.	η.	x′ (Prisms x:y).	y′.	d′ = tan ρ.
1.	c	0	(001)	24° 37′	4° 45′	1° 59′	4° 19′	1° 58′	4° 19′	0·0346	0·0755	0·0831
2.	b	0∞	(010)	0 00	90 00	0 00	90 00	0 00	90 00	0	∞	∞
3.	a	∞0	(100)	89 07	,,	90 00	,,	89 07	0 53	64·858	,,	,,
4.	l	2∞	(2$\bar{1}$0)	70 30·	,,	,,	,,	70 30·	19 29·	2·8249	,,	,,
5.	L	2$\bar{\infty}$	(2$\bar{1}$0)	107 54·	,,	,,	,,	72 05·	$\bar{1}$7 54·	$\bar{2}$·1321	,,	,,
6.	m	∞	(1$\bar{1}$0)	55 18	,,	,,	,,	55 18	34 42	1·4439	,,	,,
7.	M	∞$\bar{\infty}$	(1$\bar{1}$0)	123 30	,,	,,	,,	56 30	33 30	$\bar{1}$·5112	,,	,,
8.	n	∞2	(120)	36 08	,,	,,	,,	36 08	53 52	0·7301	,,	,,
9.	N	∞$\bar{2}$	(1$\bar{2}$0)	143 15	,,	,,	,,	36 45	$\bar{5}$3 15	$\bar{0}$·7469	,,	,,
10.	K	∞$\bar{4}$	(1$\bar{4}$0)	159 38	,,	,,	,,	20 22	$\bar{6}$9 38	$\bar{2}$·9147	,,	,,
11.	d	01	(011)	2 35·	37 20	1 59	37 24·	1 34	37 17	0·0346	0·7648	0·7628
12.	D	0$\bar{1}$	(0$\bar{1}$1)	176 46	31 28	1 59	$\bar{3}$1 32	1 41	$\bar{3}$1 25	0·0346	$\bar{0}$·6137	0·6120
13.	f	$\frac{1}{2}$0	(102)	$\bar{8}$1 16	28 42·	$\bar{2}$8 31·	4 46	$\bar{2}$8 20	4 11	0·5435	0·0834	0·5477
14.	F	$\frac{1}{2}\bar{0}$	($\bar{1}$02)	$\bar{8}$1 53	$\bar{2}$5 32	$\bar{2}$5 22·	3 52·	$\bar{2}$5 16	3 29·	$\bar{0}$·4743	0·0677	0·4776
15.	g	$\bar{1}$0	($\bar{1}$01)	$\bar{8}$5 03	46 29·	$\bar{4}$6 28	5 12·	$\bar{4}$6 16	3 35	$\bar{1}$·0525	0·0912	1·0532
16.	G	$\bar{1}$0	($\bar{1}$01)	$\bar{8}$6 31	44 28·	$\bar{4}$4 31	3 25·	$\bar{4}$4 22·	2 26	$\bar{0}$·9833	0·0598	0·9817
17.	h	11	(111)	$\bar{5}$3 26·	52 33	$\bar{4}$6 28	37 58·	$\bar{3}$9 37	28 13	$\bar{1}$·0525	0·7805	1·3057
18.	H	$\bar{1}$1	($\bar{1}$11)	$\bar{5}$2 42	50 56	$\bar{4}$4 31	$\bar{3}$6 50	$\bar{3}$8 08·	$\bar{2}$8 04	$\bar{0}$·9833	$\bar{0}$·7491	1·2319
19.	? i	1$\bar{1}$	(1$\bar{1}$1)	119 11·	50 14·	$\bar{4}$6 28	$\bar{3}$0 27·	42 09	$\bar{2}$2 01	$\bar{1}$·0525	$\bar{0}$·5880	1·2020
20.	? I	$\bar{1}$1	($\bar{1}$11)	$\bar{1}$22 37·	49 18	$\bar{4}$4 31	$\bar{3}$2 11	$\bar{3}$9 41	$\bar{2}$4 07·	$\bar{0}$·9833	$\bar{0}$·6294	1·1625
21.	r	$\frac{1}{2}\frac{1}{2}$	(112)	51 47	34 35	28 31·	23 10	26 29	20 33·	0·5435	0·4280	1·2699
22.	t	21	(211)	68 58	65 39·	64 13·	38 31·	58 15	19 05	2·0704	0·7962	2·2106

developed in the prism-zone, but the terminal faces are either lacking or so poorly developed that reflections are extremely difficult to obtain on the goniometer. The reflection signals, when obtainable, are not sharp, but are drawn out because of rounding and imperfections in the development of the faces. Examined under a high-power binocular or on the goniometer, the prism-faces are found to be finely striated, after the manner of plagioclase felspars with fine polysynthetic twinning. The result is that single clear reflection signals are uncommon when crystals are measured on the goniometer. Although more than 35 selected small crystals were measured on the goniometer, the angles fluctuated appreciably, and the angles listed in table 4 may be in error $\pm 10'$. Many of the crystals measured were 0·3 mm. or less long and 0·1 mm. wide. Small crystals were selected purposely in the hope of reducing the effects of the intricate polysynthetic twinning; but even on such minute crystals, which were water-clear, the prism-faces were striated and the terminal faces were poorly developed. The best development of terminal faces was found on the ends of the radial units of the large pink spherulite. Unlike the small spherulites, no acicular crystals projected beyond the general spherical surface of this spherulite, which consisted essentially of the terminal facets of the radiating crystals. Examined under a high-power binocular, these facets were seen also to be striated; but in many cases more coarsely so than was the case with the small crystals. A number of these facets were broken off from the spherulite and served for both optical and crystallographical measurements.

The crystallographical measurements were all made on a Goldschmidt two-circle goniometer with reducing attachment and a strong concentrated filament light source. From the averages of the weighted measurements thus obtained the crystallographical elements were computed; in addition, all observed position angles were plotted in gnomonic projection and the most probable positions of the several faces were ascertained graphically. On the crystals certain faces are invariably present; others less frequently. In table 5 are listed the faces that were found on each one of the 31 crystals measured on the goniometer. It was difficult in certain cases to decide whether a given face belonged to the crystal in normal position or to one of the intercalated twins.

The angle between the faces (100) and (010) is 89° 07′; this angle is so nearly equal to 90° that when twinning occurs with the twinning-

TABLE 5. *Observed faces on crystals of bultfonteinite.*

No.	(100)	(010)	(001)	(110)	(1$\bar{1}$0)	(120)	(1$\bar{2}$0)	(1$\bar{4}$0)	(210)	(2$\bar{1}$0)	(101)	($\bar{1}$01)	(102)	($\bar{1}$02)	(011)	(0$\bar{1}$1)	(111)	(1$\bar{1}$1)	($\bar{1}$11)	($\bar{1}\bar{1}$1)	(112)	(211)
1.	×	×	–	×	–	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2.	×	×	–	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
3.	×	×	–	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4.	×	×	×	×	×	×	×	–	–	–	–	–	–	–	–	×	–	–	–	–	–	–
5.	×	×	–	–	×	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–
6.	×	×	–	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7.	×	×	–	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
8.	×	–	–	×	–	–	×	–	–	×	–	–	–	–	–	–	–	–	–	–	–	–
9.	×	×	–	×	–	–	×	×	–	×	–	–	–	–	–	–	–	–	–	–	–	–
10.	×	×	–	×	×	×	–	–	–	–	–	×	×	–	–	–	–	–	–	–	–	–
11.	×	×	–	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
12.	×	×	–	×	×	–	×	–	–	×	–	–	–	–	–	–	–	–	–	–	–	–
13.	×	×	×	×	×	×	–	–	–	–	–	–	×	–	–	–	–	–	–	–	–	–
14.	×	×	–	–	–	–	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
15.	×	×	–	–	×	×	–	×	–	×	–	–	–	–	–	–	–	–	–	–	–	–
16.	×	×	–	–	–	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
17.	×	×	–	–	–	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
18.	×	×	–	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
19.	×	×	–	–	–	×	×	–	–	–	–	–	×	×	–	–	–	–	–	–	–	–
20.	×	×	×	–	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
21.	×	×	×	×	×	×	×	–	×	–	–	–	–	–	–	–	–	–	–	–	–	–
22.	×	×	×	×	×	×	×	–	–	–	–	–	×	×	–	–	–	–	–	–	–	–
23.	×	×	×	×	×	×	×	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
24.	×	×	×	×	×	×	×	–	×	–	–	–	–	–	–	–	–	–	–	–	×	–
25.	×	×	×	–	–	×	×	–	–	–	×	–	–	–	×	–	×	–	×	–	–	–
26.	×	×	×	×	–	×	–	–	–	–	×	–	–	–	×	×	–	–	–	–	–	–
27.	×	×	×	–	×	–	×	–	–	–	–	–	–	–	×	–	–	–	×	–	–	–
28.	×	×	×	–	×	×	×	–	–	–	–	×	–	–	×	–	–	–	×	×	–	–
29.	×	×	×	–	–	×	×	–	–	–	×	–	–	–	×	–	×	–	×	–	–	×
30.	×	×	×	–	–	×	–	–	–	–	×	–	×	–	×	–	×	×	×	×	–	–
31.	×	×	×	×	–	×	–	–	–	–	×	–	–	–	–	–	×	–	–	–	–	–

axis normal either to (100) or to (010) the face in twinning position almost coincides in position with the second pinacoid, with the result that the faces are finely striated and do not yield good reflection signals even on the most minute crystals. Twinning actually does occur on both faces and the result is commonly an interpenetrating polysynthetically twinned group in which lamellae of four different crystallographic orientations can be distinguished optically when examined in convergent polarized light or on the Fedorov universal stage.

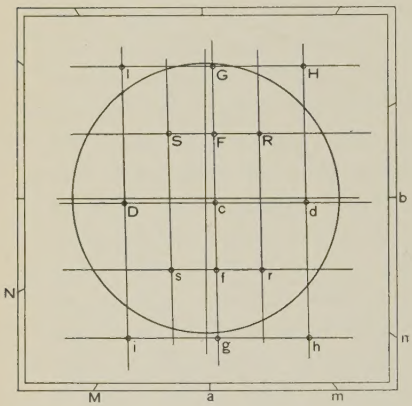

FIG. 1.

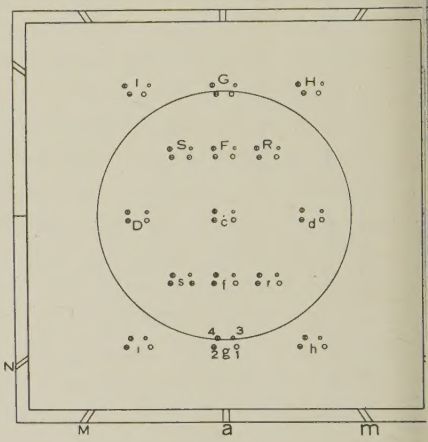

FIG. 2

FIG. 1. Observed crystal-forms of bultfonteinite in gnomonic projection.

FIG. 2. Gnomonic projection of the crystal-forms of bultfonteinite in the normal position and in the three twinning positions.

Cleavages parallel to (100) and (010) are fairly good. It is difficult to determine the degree of perfection of the cleavage because of the minute size of the prisms, the polysynthetic twinning, and the nearly parallel growth of the crystals. The fracture is conchoidal. Lustre vitreous. Hardness $4\frac{1}{2}$.

The positions of the several crystal-forms are shown assembled in gnomonic projection in fig. 1. As a result of the interpenetrating polysynthetic twinning and the near approach of the angles, (100) : (010), (001) : (100), and (001) : (010), to a right angle there appear clustered around each face in the projection the corresponding twinning positions of the face, as shown in fig. 2; thus for the face g(101), the larger clear circle, labelled 1, marks the position of the

face in undisturbed position; the circle 2 with the horizontal diameter is the face in twinning position, the twinning-plane being (010). The circles 3 and 4 show the positions of the ($\bar{1}$01) faces brought into twinning positions by twinning on the front pinacoid (100). On any single crystal not all the faces shown in figs. 1 and 2 were observed; but the optical tests show the four interpenetrating

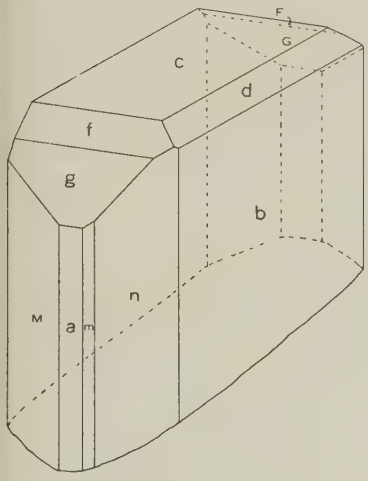

FIG. 3.

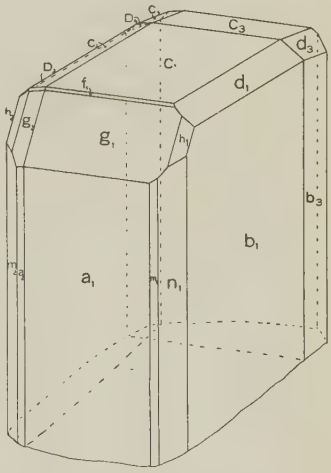

FIG. 4.

FIG. 3. Crystal of bultfonteinite as it would appear if twinning were not present and if the several faces were well developed.

FIG. 4. Crystal of bultfonteinite showing faces on crystal in normal position and other faces in twinning positions to them.

polysynthetically twinned groups so well that on a single crystal the four positions of the optical ellipsoid could be satisfactorily ascertained with the aid of a Fedorov stage. By themselves and before the optical data had been obtained the effort to disentangle the crystal-angle values of measurement was unsuccessful. Had the crystal been opaque the determination of the crystal system and especially of the character of the twinning would not have been possible.

The general development of the crystals is shown in figs. 3 and 4, in which the upper portion of the acicular prisms only is given. Fig. 3 illustrates a crystal as it would appear were it not twinned; fig. 4 shows the positions of the faces in a polysynthetically twinned crystal. The terminations represented in the figures are too sharply

drawn to be a correct illustration of the actual end faces of the greater number of crystals. However, the facets of the crystals exposed on the surface of the large pink spherulite are in part clean cut and appear as indicated in figs. 3 and 4. The terminal faces on the small acicular crystals are so poorly developed that it is only with great difficulty that reflection signals can be obtained from them on the goniometer.

This imperfect development of the end faces is probably due to the fine polysynthetic twinning and consequent near approach of the several twinned faces to a common position, so that no one of the faces could develop properly and only a general roughness resulted. In the prism-zone the conditions are different; only two sets of directions, instead of four, are brought near together by the twinning and give rise, as in the plagioclase felspars, to twinning-lamellae and fine striations, but not to the rough, imperfect development noted on the end faces. When the crystallographical measurements were first undertaken, the rough end terminations on the minute crystals were considered to be the result of later attack and etching by circulating solutions from which the sulphate crystals were deposited. This may also have been a factor, but the fact that the prism-faces showed no evidence of attack and are sharply defined makes it probable that subsequent etching was not the only factor. Against this view may, however, be cited the much better terminal development in the larger crystals of the pink spherulite, which may have been formed under conditions somewhat different from those of the small colourless spherulites.

Optical determinations.—It might be supposed that optical measurements on water-clear crystals, even though they measure only a few tenths of a millimetre in thickness and a millimetre in length, would be a simple task. In the present case, however, the intricate polysynthetic twinning on two planes, approximately at right angles one to the other and so fine that satisfactory interference-figures in convergent polarized light are extremely difficult to obtain, renders the task unusually trying and time-consuming. Had it not been for the Fedorov stage methods, it is doubtful that satisfactory results could have been obtained.

Under the microscope the mineral exhibits medium refringence, medium birefringence, and fine polysynthetic twinning-lamellae. The acicular crystals exhibit, parallel with the prism-axis, fine twinning-lamellae with high extinction-angles. The extinction-angle on

(010) is $c:\gamma' = 27°$ to $29°$; on (100) $c:\gamma' = 46°$ to $48°$. Flakes normal to the prism-axis show two sets of interpenetrating twinning-lamellae crossing nearly at right angles as in microcline. In convergent polarized light the interference-figures that can be obtained are, in general, unsatisfactory. On sections nearly normal to the prism-axis an optic axis may be seen in the field; the axial bar is slightly curved and points toward γ as acute bisectrix. The optic axial angle, ascertained on sections of this kind by measuring the angle between the bisectrix and the optic axis, was found to be approximately $2E = 130°$. Dispersion of the optic axes is barely perceptible with $2V_r > 2V_v$ apparently. On a section nearly normal to the optic axes, the plane of the optic axes includes an angle of approximately 47° with the traces of the twinning-lamellae. The optical sign is positive.

The refractive indices were measured in sodium-light both by the immersion method and on an Abbe crystal refractometer on polished plates cut from the large spherulite. On these plates the maximum and minimum refractive indices were found to be, for sodium-light, $\alpha = 1{\cdot}587 \pm 0{\cdot}002$, $\gamma = 1{\cdot}597 \pm 0{\cdot}002$. Many attempts were made to measure β by the immersion method; but they were not successful because of the intricate twinning phenomena. The refractive index, β, was found, on computation from the optic axial angle and the refractive indices, α and γ, to be $\beta = 1{\cdot}590$. The principal birefringences from these values are: $\gamma - \alpha = 0{\cdot}010$, $\gamma - \beta = 0{\cdot}007$, $\beta - \alpha = 0{\cdot}003$.

Measurements with the aid of the Fedorov stage were made on a number of sections; at first on thin sections cut from the large spherulite approximately normal to the radiating group. Experience soon proved that, although some measurements could be obtained on these sections, the lack of satisfactory crystal outlines and of the possibility of determining the crystal orientation on a given section would prevent this method from obtaining the desired data. The effort was then made to mount small definitely oriented crystals and to grind and polish thin plates normal to the prism-axis. This method failed because of the minute size of the crystals. Recourse was then had to a special instrument devised for the purpose. This apparatus is shown in fig. 5 (actual size) in which A is the side view in section, B the front view, and C the plan or top view. The device is made from a block M of brass, on top of the upright end of which a straight bronze spring a is clamped by a screwed brass plate k. At the inner end of this spring a brass angle piece is attached by

a screwed brass plate *d*. To the upright side of the angle piece a section of a razor-blade *c* is clamped by a second screwed brass plate. When the spring is raised and then released, the razor-blade strikes a sharp blow against the smooth upper surface of the brass support. The apparatus is enclosed by plates of microscope object glass (25 × 46 mm.) cemented to the brass support *M*; in addition, the top is

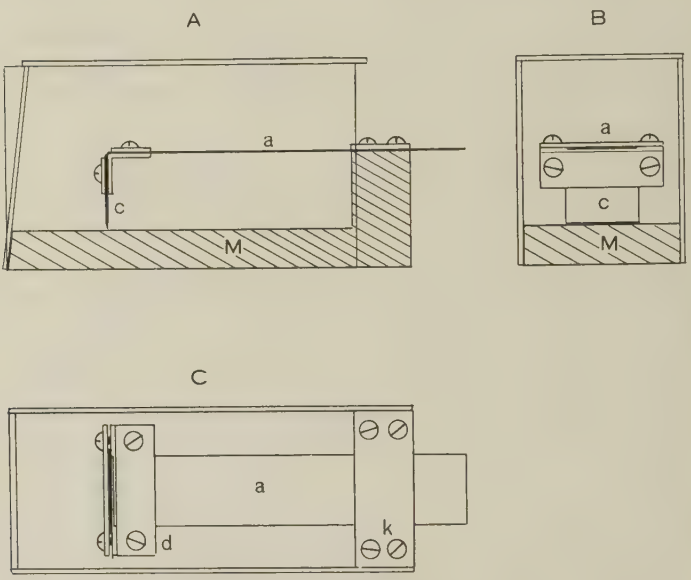

Fig. 5. Apparatus for splitting off thin flakes of a crystal normal to its prism-axis. A is the side view, B front view, and C plan.

covered by a similar glass plate and held in position by the observer during the operation. The plates prevent the escape and loss of the minute crystal flakes chipped off by the razor-blade.

The small crystal from which sections are to be split off normal to the axis is now placed with its prism-axis normal to the razor-blade and underneath its edge. All these operations are done under a binocular magnifying 20 diameters. The top glass plate is now placed in position. The razor-blade is raised slightly with the aid of a small screw-driver or rod placed under the angle plate at *d*, and supported, as a lever, at *k*. The screw-driver is withdrawn slightly and the spring released. The razor-blade descends rapidly, like a guillotine, and decapitates or chips off a thin flake normal to the prism-axis of the crystal. After some practice it was found that

several sections, retaining the complete outline of the prism-zone, could be obtained by this method from a single crystal.

A suitable section was then mounted on the Fedorov stage and the positions of its principal optical directions with reference to the crystallographical directions were measured. Twenty-three crystal sections were thus measured. Many other sections were mounted, but were discarded for one reason or another. On several of the

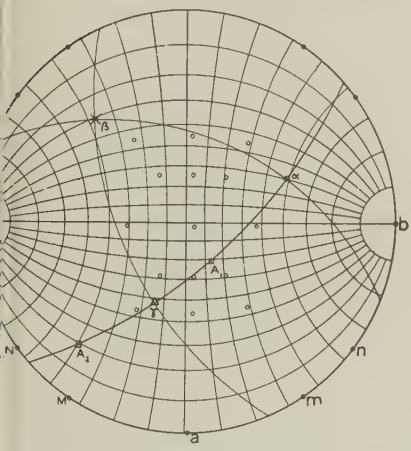

Fig. 6.

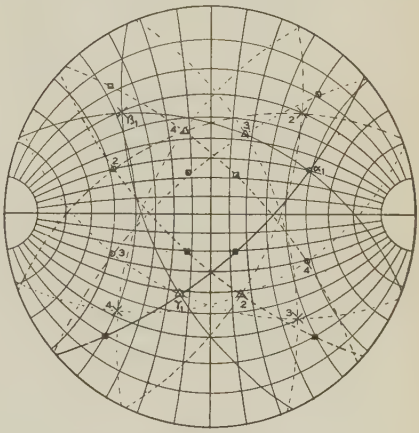

Fig. 7.

Fig. 6. The principal optical directions and crystal-faces of bultfonteinite in stereographic projection.

Fig. 7. Stereographic projection of the principal optical directions in a bultfonteinite crystal in normal position and in the three twinning positions.

sections the optical orientation of all four twinning-lamellae could be measured. The results of the measurements are listed in table 6. The positions of the principal optical directions thus measured with reference to the crystallographical directions are shown in stereographic projection in figs. 6 and 7. In fig. 6 the directions are given for the single crystal ; in fig. 7 the positions of the principal optical directions in the four different twinning-lamellae are plotted.

Table 6. *Angular positions of principal optical directions in bultfonteinite.*

	ϕ.	ρ.	ξ_0.	η_0.	ξ.	η.
α	$\bar{2}4°$ 00′	55° 00′	$\bar{3}0°$ 00′	52° 30′	$\bar{1}9°$ 00′	48° 30′
β	$\bar{1}32$ 30	66 00	$\bar{5}9$ 00	$\bar{5}6$ 30	$\bar{4}2$ 30	38 00
γ	111 00	44 30	42 30	$\bar{1}9$ 30	41 00	15 00
A_1	57 30	24 30	21 00	14 00	20 30	13 00
A_2	131 00	75 30	71 00	$\bar{6}8$ 30	47 00	$\bar{3}9$ 30

The results of the measurements of the optic axial angle on different sections by the Fedorov stage method in white light are listed in table 7. In each case only the angle between an optic axis and γ or

TABLE 7. *Measurement of half the optic axial angle of bultfonteinite.*

No.	V.	No.	V.	No.	V.	No.	V.
2	34·0°	9	37·5°	16	40·0°	20	35·0°
3	35·0	10	33·0	17	37·5	21	39·0
4	33·0	11	34·0	18	40·0	22	31·0
5	38·0	12	34·0	19	31·0	,,	37·5
6	34·0	13	38·0	,,	35·0	23	38·0
7	34·5	14	32·0	,,	34·0		
8	35·5	16	37·5	,,	28·0		

a could be obtained. At steeply inclined positions of the sections the twinning-lamellae overlapped to such a degree that measurements were not possible. The weighted average of these values is $V = 35°$, $2V = 70°$, and $2E = 132°$.

Comparison with other fluorine-bearing hydrous calcium silicates.— Two other minerals, custerite[1] and zeophyllite,[2] have chemical compositions that bear some resemblance to that of bultfonteinite. The compositions and other data on these minerals and also on hillebrandite[3] are assembled in table 8.

The formula for custerite is commonly written Ca_2HFSiO_4; it may, however, be written $CaO.Ca(OH,F)_2.SiO_2$. In this form its resemblance to the formulae for hillebrandite, $CaO.Ca(OH)_2.SiO_2$, and bultfonteinite, $2Ca(OH,F)_2.SiO_2$, is apparent. In custerite part of the hydroxyl, OH, of hillebrandite is replaced by fluorine. In custerite and hillebrandite half of the calcium oxide is still intact, the oxygen of the second half being replaced by OH and F; whereas in bultfonteinite none of the CaO remains as such, the calcium being entirely taken up by OH and F.

These three minerals show with phenolphthalein a strong alkaline reaction, indicating the presence, in aqueous solution, of calcium hydroxide. The minerals are easily soluble in hydrochloric acid. Afwillite, whose formula may be written $3Ca(OH)_2.2SiO_2$, exhibits similar chemical behaviour.

The mineral zeophyllite, on the other hand, bears little resemblance

[1] J. B. Umpleby, W. T. Schaller, and E. S. Larsen, Amer. Journ. Sci., 1913, ser. 4, vol. 36, pp. 385–394.

[2] A. Pelikan, Sitzungsber. Akad. Wiss. Wien, Abt. 1, 1902, vol. 111, p. 334; also F. Cornu, Min. Petr. Mitt. (Tschermak), 1905, vol. 24, p. 127.

[3] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, pp. 551–553.

TABLE 8. *Comparison of bultfonteinite with other hydrous calcium silicates.*

	Bultfonteinite.		Custerite.		Hillebrandite.		Zeophyllite.	
	%	Molec. ratios.	%	Molec. ratios.	%	Molec. ratios.	%	Molec. ratios.
SiO_2	26·50	0·441	32·17	0·536	32·59	0·540	38·84	0·647
Al_2O_3 }	0·72	0·006	—	—	0·23	0·002	1·73	0·017
Fe_2O_3 }			—	—	—	—	0·10	0·001
Fe_3O_4	—	—	1·00	0·004	0·15	0·001	—	—
MgO	—	—	1·19	0·030	0·04	0·001	0·17	0·004
CaO	54·20	0·967	55·11	0·984	57·76	1·030	44·32	0·791
Na_2O	—	—	—	—	0·03	0·001	0·38	0·006
K_2O	—	—	—		0·05	0·001	0·24	0·003
H_2O	13·36	0·741	5·30	0·294	9·36	0·502	8·98	0·499
F	8·81	0·464	8·12	0·427	none	—	8·23	0·433
TiO_2, MnO	—	—	—	—	0·03	—	—	—
	103·59		102·89		100·24		102·99	
Less O for F	3·71		3·42				3·47	
	99·88		99·47				99·52	
Formula	$2Ca(OH,F)_2.SiO_2$		$CaO.Ca(OH,F)_2.SiO_2$		$CaO.Ca(OH)_2.SiO_2$		$Ca_4H_4F_2Si_3O_{11}$	
Specific gravity ...	2·73		2·91		2·69		2·76	
Hardness	$4\frac{1}{2}$		5		5–6		3	
Fusibility	Difficult		Difficult		Difficult		Easy	
Cryst. syst.	Triclinic		Monoclinic		Orthorhombic		Rhombohedral-tetartohedral	
Cleavage	(010), (100)		(001), (110)		(110) ?		(0001)	
Twin-plane	(010), (100)		(001)		—		—	
Refrac. indices α	1·587 ± 0·002		1·586 ± 0·005		1·605 ± 0·005		—	
Refrac. indices β	1·590 ± 0·002		1·589 ± 0·005		—		-	
Refrac. indices γ	1·597 ± 0·002		1·598 ± 0·005		1·612 ± 0·003		1·55	
Optic axial angle 2V ...	70°		60°		—		—	
Optic axial angle 2E ...	132°		105°		60 − 80°		0 − 27°	
Optical sign	positive		positive		negative		negative	
Dispersion of optic axes	weak		rather strong		—		—	
Optical orientation ...	Triclinic		$b = a$, $a : \gamma = 6{\cdot}5°$		$c = \gamma$		$c = \epsilon$	

either in chemical behaviour or in its optical and other properties with custerite and bultfonteinite. In composition it appears to be a solution of $4CaO.3SiO_2$ and $4Ca(OH,F)_2 3SiO_2$ in the proportion of 1 to 7 approximately.

The refractive indices and the birefringences of bultfonteinite and custerite are identical, within the limits of error; both minerals are

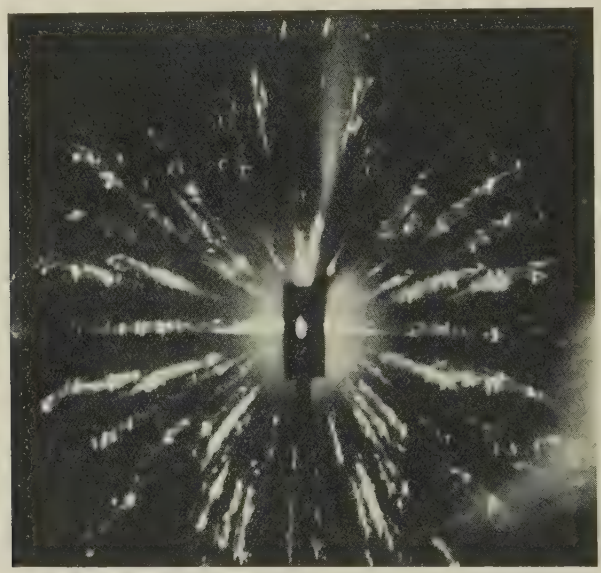

FIG. 8. X-ray diffraction pattern of a prismatic fragment of bultfonteinite.

biaxial, optically positive with approximately equal optic axial angles. However, the extinction-angles and other relations between crystallographical and optical properties are so different that the two minerals can be readily distinguished under the microscope. Hillebrandite is orthorhombic and resembles neither custerite nor bultfonteinite in its optical and crystallographical properties.

X-ray photograph of bultfonteinite.—The photograph, fig. 8, was taken by, and through the courtesy of, Mr. H. S. Roberts of the Geophysical Laboratory. The crystal diffraction pattern of fig. 8 was obtained by rotating a prismatic sliver from the pink spherulite in the axis of the X-ray apparatus. The effect of the twinning is clearly shown in this photograph; but the relations are so complex that no effort was made to analyse the photograph critically.

On the changed composition of an anorthoclase-bearing rock-glass.[1]

(With Plate VI.)

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[Read March 15, 1932.]

THE present investigation began with an attempt to isolate and analyse the small sparse anorthoclase insets (phenocrysts) of the chilled glassy selvage of a felsite dike. On comparison of the compositions of the insets and the host rock it was found that the relationship was abnormal and that the insets could not have grown in a magma represented by the glass. The composition of the felsite interior of the dike, however, represents a magma which could have yielded the anorthoclase, and full consideration leads to the conclusion that the glass, though absolutely fresh and unaltered in appearance, has suffered marked changes in composition.

In east Iceland a rugged mountain ridge trending ESE. separates Faskrudsfjord from Stoðvarfjord. To the west of Sandfell (2428 feet), a prominent hill of light-coloured felsite on the Faskrudsfjord side, the ridge can be crossed at about 2000 feet by the Stoðvarskarð Pass, immediately to the east of which is a considerable development of acid lavas and tuffs including glasses and splendid spherulitic rocks, interbedded in the normal Tertiary basalts, here dipping 9° W. The acid series is at least 700 feet thick, and is petrologically distinct from the other Tertiary acid extrusives in east Iceland, in that the dominant felspar constituent is anorthoclase and not acid plagioclase.

[1] Unless otherwise stated, the chemical analyses given in this paper were made by Dr. H. F. Harwood. The remainder of the work was carried out by Dr. L. Hawkes who has written the paper.

The rocks to be described occur as an irregular vertical dike-like intrusion into the basalts below the acid extrusives, to which latter series the dike clearly belongs. At the western end of Stoðvarfjord the valley of Jafnadal leads NW. to the pass, and the specimens were taken from an exposure at about 1100 feet in the first notable tributary met on the northern side on ascending the valley. Here, abutting against the basalts, is a vertical wall 1–3 feet thick of a lustrous black glass with perlitic structure, the larger perlite ellipsoids measuring $8 \times 5 \times 3$ inches. The glass grades evenly away from the contact through a duller rock to a fine-grained grey felsite; all varieties contain anorthoclase insets averaging 1–2 mm. in length. Further exposures of the dike occur in the stream course below this locality.

The contact facies appears in thin section as a faintly brown glass crowded with microlites in fluxion parallelism, many of pyroxene averaging 0·002 mm. across, with some broader felspar. The insets are mainly anorthoclase, forming 2·8 % by volume (3·2 % by weight) of the rock, some pyroxene (0·05 % vol.) together with minute magnetites and zircons. There is some tendency to glomero-porphyritic aggregation of the four minerals. The pyroxene exhibits a very feeble pleochroism—a clear grass-green, γ slightly brownish-green; $\gamma - a$ about 0·03, $\gamma : c$ (on microlites) 55°. These properties indicate a slightly sodic pyroxene.

The anorthoclase insets are euhedral, although some are bent or fractured as a result of the differential flow accompanying the intrusion of the magma. They are short rectangular prisms elongated along the a-axis: some are tabular, parallel to (001). The forms observed were c(001), b(010), a(100), $y(\bar{2}01)$, m(110), and n(021). Cleavage, (001) dominant, (010) good, $(\bar{2}01)$ subordinate. Carlsbad, Manebach, and Baveno twinning occurs. The optic axial plane is normal to (010), and the acute bisectrix α is near the a-axis. In thin section the felspar exhibits the characteristic irregular patchy extinction of anorthoclase, particularly well marked on (001) sections which show a minute discontinuous albite twinning. Sections normal to the acute bisectrix show cross-hatching due to albite twinning together with bands parallel to the (001) edge. Cleavage flakes (010) are normal to γ and give an extinction $\alpha : (001) = 9°$; (001) cleavage flakes are nearly optic normal sections and show fine albite twinning and extinction $\alpha : (010) = 1–2°$. Refractive index $\gamma = 1·531$. Many measurements of birefringence on cleavage

flakes gave: on (010), $(\beta-\alpha) = 0{\cdot}0061 \pm 0{\cdot}0003$; on (001), (near $\gamma - \alpha$) $= 0{\cdot}0072 \pm 0{\cdot}0002$. Measurement of the optic axial angle on an acute bisectrix section gave $2E = 83° \pm 5°$; optically negative.

The glass, refractive index 1·490, shows a birefringence which is slightly enhanced in the neighbourhood of the insets, where values of 0·0012 were measured. All parts of the glassy field of each thin section extinguish simultaneously, except near the insets, where the direction of vibration of the α ray swings round, always lying normal to the boundaries of the crystals and the flow lines round them. The streaky and mottled appearance of the polarization greys (plate VI, figs. 6, 7, 9, 10) is partly due to the microlites and partly to the presence around the larger microlites of small negative birefringent fields which are small-scale reproductions of the effect noted round the insets. The orientation of the vibrations of the α ray in the neighbourhood of the insets is that which would accompany the existence of radially compressive stress around the crystals. The phenomenon can be demonstrated experimentally by adding mineral grains (but not quartz) or fragments of 'vitreosil' to melted borax and allowing the preparation to cool, when negative figures appear around each grain, the state of radial compression in the borax glass being sometimes further revealed by the growth of a system of radial cracks within the birefringent zone. The strain is due to the circumstance that on vitrification with falling temperature the contraction of the glass is greater than that of the inclusions, and, in the case of the rock-glass, of the anorthoclase.[1] The rock-glass is now no longer in a state of mechanical strain but the optical effect remains, and if the rock is crushed to pass 90 mesh the fragments will still retain their birefringence. Ninety per cent. of the water in the rock-glass can be expelled without affecting the birefringence, which latter disappears at red heat. The birefringence shown outside the influence of the insets must have some other origin and be due to stresses operating over a larger field.

It was thought that where it is unaffected by the presence of phenocrysts the birefringence of the glass as a whole would be related to the strains governing the perlitic fracturing, but examination of a thin section 77 sq. cm. in area, cut through one of the large perlite ellipsoids with concentric cracks, shows that this is not the case, for the whole field extinguishes in one position. The

[1] T. H. Waller, The phenomena of strains, etc., observable in obsidian. Geol. Mag., 1885, p. 91.

birefringence is of uniaxial negative character. We are unaware that an optical phenomenon of this kind has been noticed before, and discussion of its causation must await further study in the field.

One end of a large perlite ellipsoid is greenish-grey in colour and in thin section exhibits dark brown devitrification patches and streaks; the alteration of the latter has been guided by cracks (plate VI, fig. 8).

The felsite in section shows the same anorthoclase insets as the glass, with magnetite and zircon, but the pyroxene is represented by opaque dust, and the groundmass is holocrystalline with small felspar laths and larger quartzes which may enclose the felspar poikilitically.

The contact-rock is a favourable one for an investigation of the relationship of the composition of the first formed felspar to that of the groundmass. The insets form but 3 % of the rock and include one kind of felspar only which can be readily separated from the vitreous groundmass and other crystals. The separation was made by Mr. A. F. Hallimond, who suggested the use of his electro-magnetic separator,[1] the glass being more magnetic than the felspar. The rock was crushed to a size between 60 and 90 mesh, and 375 grams were passed through the machine to yield 4·5 grams of a white, least-magnetic product, which, after suspension in a bromoform mixture and removal of the small sunken and floating fractions, proved to be 87 % felspar, a satisfactory result considering the small size of the crystals. In table I is given the analysis of the contact-rock (no. 1), and that of the felspar separation (no. 3), and also the calculated norms.

The amount of glass present in the felspar preparation is estimated in two ways: (*a*) In the rock norm 29·26 parts of free silica are equivalent to 97 parts of glass (allowing 3 % of insets), and the felspar preparation norm gives 4·15 % free silica, which is then equivalent to $(97 \times 4{\cdot}15)/29{\cdot}26 = 13{\cdot}7$ % of glass; (*b*) the rock analysis gives 5·88 parts H_2O+ in 97 parts of glass, and 0·71 % H_2O+ in the felspar preparation is then equivalent to $(97 \times 0{\cdot}71)/5{\cdot}88 = 11{\cdot}7$ % glass. Adopting a figure of 13 %, this proportion of no. 2 was subtracted from no. 3, and the result recalculated to 100 % is given in no. 3 *a*, which is then the composition of the anorthoclase with the glass eliminated. Removing the non-felspathic constituents

[1] A. F. Hallimond, An electro-magnetic separator for mineral powders. Min. Mag., 1930, vol. 22, p. 377.

TABLE I.

	1.	1*a*.	2.	3.	3*a*.
SiO_2	70·55	76·19	77·77	66·30	65·48
Al_2O_3	11·82	12·76	11·61	18·86	19·86
Fe_2O_3	0·55	0·59	0·79	0·23	0·18
FeO	1·06	1·14	0·40	0·20	0·07
MgO	0·03	0·03	trace	none	—
CaO	0·74	0·80	0·33	1·16	1·22
Na_2O	5·08	5·49	3·91	6·95	7·21
K_2O	2·58	2·78	4·34	4·97	5·31
$H_2O-(110°)$	1·40	—	0·06	none	—
$H_2O+(110°)$	5·88	—	0·56	0·71	—
CO_2	0·03	0·03	none	—	—
TiO_2	0·09	0·10	0·09	—	—
P_2O_5	trace	—	0·02	—	—
Cl	trace	—	trace	—	—
S	trace	—	0·01	—	—
MnO	0·04	0·04	0·02	trace	—
SrO	trace	—	none	0·04	0·05
BaO	0·03	0·03	0·02	0·54	0·62
Li_2O	none	—	trace	—	—
NiO	none	—	none	—	—
F	0·04	0·04	—	—	—
	99·92	100·02			
O less F	0·02	0·02			
	99·90	100·00	99·93	99·96	100·00
Specific gravity ...	2·307	—	2·565	2·584	—
Norms.					
Quartz	29·26	31·56	38·35	4·15	0·51
Orthoclase	15·23	16·43	25·68	29·41	31·42
Albite	42·92	46·29	33·06	58·74	60·88
Anorthite	1·78	1·92	1·39	4·45	4·86
Celsian	—	—	—	1·31	1·53
Strontium-felspar ...	—	—	—	0·13	0·14
Hypersthene	0·60	0·65	—		—
Diopside	1·67	1·80	—	0·73	0·41
Ilmenite	0·17	0·18	0·15	—	—
Magnetite	0·79	0·85	1·16	0·32	0·23
Symbols	I. ″4.1.4.	—	I. 3(4).1.3″.	—	—

1. Glassy contact facies of the dike. Jafnadal, Stoðvarfjord, Iceland.

1*a*. Analysis no. 1 recalculated to 100 %, with water eliminated.

2. Felsite. Interior of the Jafnadal dike.

3. The separation (containing 87 % of anorthoclase insets) obtained from the rock-glass no. 1.

3*a*. The composition of the anorthoclase insets, being no. 3 recalculated after subtraction of 13 % of no. 1.

from the norm of no. 3*a*, the composition of the anorthoclase becomes:

Albite	61·60
Orthoclase	31·80
Anorthite	4·90
Celsian	1·55
Strontium-felspar ...	0·15
	100·00

This is the composition of a normal potash-rich anorthoclase with 32 Or, 68 Ab + An. From his study of the Ab + An + Or of anorthoclases Vogt finds 32 to be the maximum recorded percentage of Or.[1] The felspar shows a notable content of baryta present as celsian which is known as a constituent of many anorthoclases.[2] Comparison of the baryta content of the felspar (0·62 %) with that of the whole rock (0·03 %) shows that 0·019 %—more than half of the baryta of the magma—has entered into the first 3·2 % of the rock to crystallize. The specific gravity of the anorthoclase, being that of the separated product recalculated to eliminate 13 % of glass, is 2·63, a value which is probably a little too high owing to the glomero-porphyritic tendency of pyroxene and magnetite to accompany the felspar.

Comparing the composition of the felspar with that of the whole rock, and considering the alkalis, the surprising result is obtained that the rock rich in soda bears insets relatively richer in potash, so that differentiation appears to be proceeding towards a soda-rich rest magma. This runs counter to the general rule deduced by Vogt from consideration of a great mass of data, that, in acid magmas with small contents of anorthite and an orthoclase content of less than about 40 % of the Ab + An + Or, the first formed felspar is poorer in orthoclase than the magma.[3] The figures for the insets and the rock are given in table II (nos. 1 and 2), and to demonstrate the abnormality of their relationship both as regards alkalis and lime, they are plotted on fig. 1, which is a copy of part of Vogt's

[1] J. H. L. Vogt, The physical chemistry of the magmatic differentiation of igneous rocks. II. On the felspar diagram Or : Ab : An. Skrifter Norske Vidensk.-Akad. I. Mat.-nat. Kl., Oslo, 1926, no. 4, p. 28. [Min. Abstr., vol. 3, p. 379.]

[2] N. Orlow, Analysen einiger Silikate aus der Gegend von Pjatigorsk. Neues Jahrb. Min., 1912, vol. 1, p. 421.

D. Beliankin, Contribution à la chimie des feldspaths. Bull. Acad. Sci. U.S.S.R., 1929, p. 571. [Min. Abstr., vol. 5, p. 70.]

[3] J. H. L. Vogt, loc. cit., p. 82.

diagram illustrating the relationships between the first-formed felspars and their host rocks.[1]

TABLE II. The calculated relative proportions of Or, Ab, An, in (1) the anorthoclase insets, (2) the glassy contact-rock, (3) the holocrystalline interior felsite.

	1.	2.	3.
Orthoclase ...	32·3	25·4	42·7
Albite	62·7	71·6	55·0
Anorthite... ...	5·0	3·0	2·3
	100·0	100·0	100·0

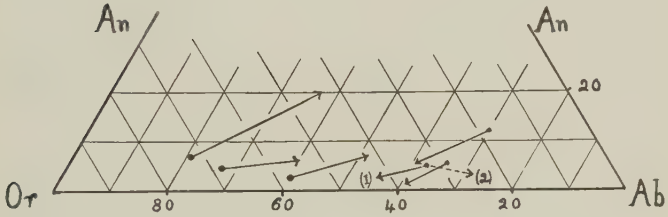

FIG. 1. Felspar diagram adapted from Vogt. The arrow-heads indicate the Or, Ab, An ratios of the rocks, and the dots to which they are joined the ratios of their respective insets. Arrow-head (1) indicates the ratios of the interior felsite, and (2) those of the contact facies of the Jafnadal dike, the dot to which they are joined representing the composition of their anorthoclase insets.

To ensure that no analytical error was responsible for these results, Iceland was revisited, and another sample of the glass obtained, from which 1·1 gram of felspar was separated magnetically as before and analysed, giving:

	Felspar separation.	Rock.
Na_2O	6·88	5·07
K_2O	4·89	2·54

These figures substantiate those previously found.

The clue to the solution of the problem is given by a comparison of the analyses of the felspar and the dike interior felsite (table I, no. 2), for the anorthoclase now appears as a normal first-formed constituent of the felsite magma, as is seen when the results (table II, no. 3) are plotted on the diagram (fig. 1). The orthoclase content of the felsite is rather greater than the 40 % given by Vogt as the upper limit for rocks yielding felspars richer in soda than themselves,

[1] J. H. L. Vogt, loc. cit., fig. 10, p. 81.

but the data are not sufficiently precise to permit a very exact determination of the eutectic point. We conclude, then, that the magma of the dike rocks contained about 3 % of insets—mainly anorthoclase, and that it had the composition of the felsite, and that the differences between the analyses of the felsite and chilled contact glass are due to subsequent changes in the composition of the latter.

The hypothesis that the composition of the glass has remained unchanged and that the insets were introduced into the liquid (now glass) as the result of crystal settling from another magma is rejected on the following grounds: (1) It has not yet been demonstrated that settling of such small felspars—some are 0·2 mm. across—does occur in acid magmas; (2) the insets are evenly distributed throughout the rock; (3) the insets are euhedral, and there is no resorption or overgrowth to indicate that they have existed out of equilibrium with their liquid environment; (4) the proportion of insets in the glass is the same as that in the felsite; (5) the abnormal rock is restricted to the glassy facies. Both this and (4) would be highly fortuitous circumstances on the settling hypothesis. (6) The contact-rock, as is to be expected if soda has replaced potash, is abnormal in that with marked excess of soda over potash (2·50 %) there is a small content of lime (0·74 %). In fig. 2 are shown the lime contents of all (27) those analysed acid rocks from the British and Icelandic Tertiary province with soda in excess of potash. All those rocks are included which have more than 66 % of silica, and soda in excess of potash by any amount up to 3 %. The diagram shows that with increasing excess of soda the minimum contents of lime rise, and that no rock of the Jafnadal type is known in the province. Whereas none of these criteria is in itself conclusive the cumulative evidence is decisive, and there are no grounds for rejecting the most straightforward view that the glassy facies is derived from the same liquid, which in the interior of the dike has crystallized to form the felsite.

We pass to a consideration of the considerable water content shown by the glass. The amount of water which can be held in solution in magma is governed by pressure and temperature, diminishing with decreasing pressure and with increasing temperature. From Goranson's data[1] we discover that the water found in the glass (H_2O+ 5·88 %) could, between the temperatures of 700 and

[1] R. W. Goranson, The solubility of water in granite magmas. Amer. Journ. Sci., 1931, ser. 5, vol. 22, p. 481.

900° C., be held by an acid magma at depths not less than between 3–4 km. The Jafnadal dike is petrologically allied to the acid extrusives above it, and there can be little doubt that it was emplaced at the time when the surface of the country was at or near the top of the acid extrusive series. A half kilometre is a liberal estimate of the original depth below the surface of the glass analysed —at which depth the maximum possible water content at 900° is

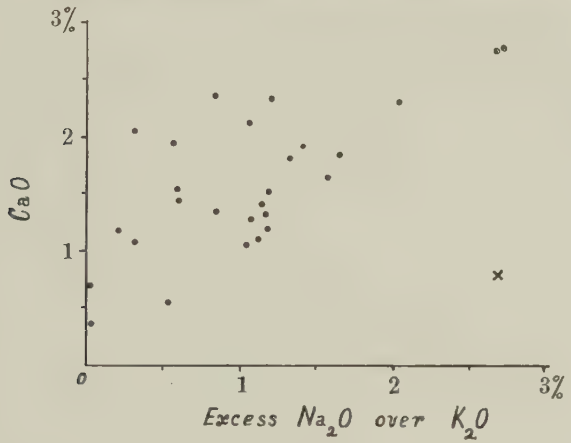

Fig. 2. The lime contents of the acid rocks of the North Atlantic province plotted against the excess of soda over potash. The cross gives the relationship for the Jafnadal contact-glass.

about 1 %. Had the temperature of the magma on intrusion been as low as 700° the water content could not have been more than 2 %, so it is clear that the bulk of the water now in the glass was not held in the magma on emplacement, but has been added later. An even more striking case is that of the glass which outcrops at the Stoðvarskarð Col, for this is the upper part of an acid lava flow which in its original liquid form can have held only a negligible amount of water, whereas the rock now shows H_2O+ 6·92 %.

The capacity of glass for water increases with falling temperature, and it would be reasonable to suppose that the water was added from the interior of the dike or lava, from which it was expelled on crystallization, and that the other changes in composition were effected at the same time. In this connexion we may note that the glassy casing of the Stoðvarskarð acid lava (also with anorthoclase

insets) gives K_2O 2·50 %, Na_2O 3·63 % (L. H. anal.), or Or : Ab 33 : 67. The optical properties of the inset anorthoclase are the same as those of the analysed felspar, and if their compositions are the same this extrusive glass as compared with the contact dike rock has suffered a similar but smaller alkali exchange.

To further compare the felsite and glass compositions the latter is recalculated to a water-free basis (table I, no. 1 *a*). The notable differences remaining for consideration are those relating to silica and alumina. The excess of silica in the felsite is 1·58 %, but it is the normative free silica which is significant, and this shows an excess in the felsite of 6·79 %. Recalculation of the felsite norm after replacement of potash by soda to give the proportions present in the glass shows that about 7 % of free silica has been extracted—one may surmise in water solution. This silica loss accounts for the increased alumina of the glass.

That the changes in composition have been effected in the glass and not in the crystalline felsite is in accordance with the fact that 'glass in general has a lower resistance towards chemical agencies than mineral of the same composition'.[1] In many cases changes in the glass are accompanied or succeeded by devitrification, as is exemplified in a rock from Borgarfjord, east Iceland, in which unaltered spherulites occur in a groundmass exhibiting perlitic marking, but which is composed of a mosaic of quartz crystals (figs. 3 and 4), and a similar example of this selective silicification is provided by the well-known spherulitic rock of Lea, Shropshire. It is not as a rule difficult in the case of a crystalline rock to detect alteration when this has occurred, but the example given in this paper shows that a rock-glass which neither macroscopically nor microscopically shows the slightest trace of alteration—even retaining the strain polarization set up on vitrification—has yet suffered considerable changes in composition, viz. loss of silica, addition of water, and replacement of potash by soda.

Fenner gives an example of a basic pillow lava in the 'nearly unaltered' glassy skin of which potash has replaced soda, and 'these results make one dubious whether any basaltic or doleritic glass, if not of absolutely fresh appearance, can be assumed to have the composition it had at the beginning'.[2]

[1] J. H. L. Vogt, loc. cit., III (second half), 1931, p. 192.

[2] C. N. Fenner, The residual liquids of crystallizing magmas. Min. Mag., 1931 vol. 22, p. 556.

Not only by reason of its instability, but also from the circumstances governing its formation, rock-glass is especially liable to attack, for it seldom occurs as a single intrusive mass, but predominantly as a chilled casing of a larger enclosed volume of magma, and this on crystallization releases products to the action of which the glass must be subject. Petrologists attach great importance to the apparently unaltered chilled glassy facies as

FIG. 3.

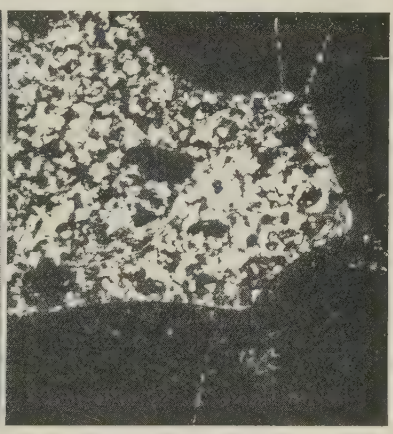

FIG. 4.

FIG. 3. Spherulitic rhyolite from the Helgá valley, Borgarfjord, east Iceland. Between the curved borders of the spherulites lies an area with perlitic markings. Ordinary light, ×25.

FIG. 4. The same between crossed nicols. The perlitic area is seen to be composed of a mosaic of granular quartz.

representing the original intruded magma—being undisturbed by crystallization-differentiation, but caution is necessary, and to Bowen's statement [1] 'They [i.e. glassy rocks] are the only rocks of which we can say with complete confidence that they correspond in composition with a liquid', we would add 'provided their composition has remained unchanged'. In the field, glasses have a deceptively fresh appearance as compared with the crystalline rocks, but to discover the original composition of the liquid it is safer to take the fine-grained holocrystalline contact-rock, rather than a glass.

In his study of the dacite mass of Hamarfjord, east Iceland, the

[1] N. L. Bowen, The evolution of igneous rocks. 1928, p. 125.

author (L. H.) in order to arrive at the composition of the original magma took the fresh glassy casing for analysis, the alkalis found being Na_2O 4·27 %, K_2O 1·59 %.[1] In the light of the present investigation this result was reviewed with suspicion, especially as the lime content of the rock is low (1·85 %). Accordingly, the alkalis of the finely crystalline dacite have now been determined with the following result: Na_2O 4·60, K_2O 2·96 %, showing that here also alkali exchange has occurred in the glass.

We make acknowledgement to Mr. A. F. Hallimond for his separation of the anorthoclase insets.

Explanation of Plate VI.

Fig. 5. The analysed contact-rock, Jafnadal dike, Iceland. Anorthoclase insets in glass with microlites. Ordinary light, ×10.

Fig. 6. The same between crossed nicols, the cross-lines marking the planes of vibration of light through the nicols. The glass in this position exhibits the maximum birefringent effect.

Fig. 7. The same. The crossed nicols have been rotated through 45° to show the main body of the glass in extinction, and light patches due to local strain at the insets.

Fig. 8. The Jafnadal dike contact-rock. Anorthoclase inset in glass with microlites in fluxion parallelism to the inset boundary. The black streaks represent brown devitrification bands. Ordinary light, ×33.

Fig. 9. The same between crossed nicols. The cross-lines mark the planes of vibration of light through the nicols. The patchy birefringence shown in the glass near the inset is due to strain. The white streaks mark the devitrified bands.

Fig. 10. The same. The crossed nicols have been rotated through 45°. Comparison with fig. 6 shows that in the glass the plane of polarization of one ray (α) lies normal to the boundary of the inset and to the flow-lines.

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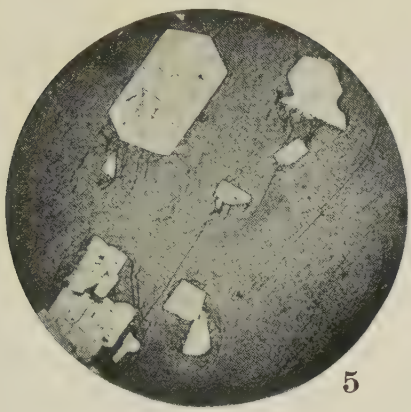
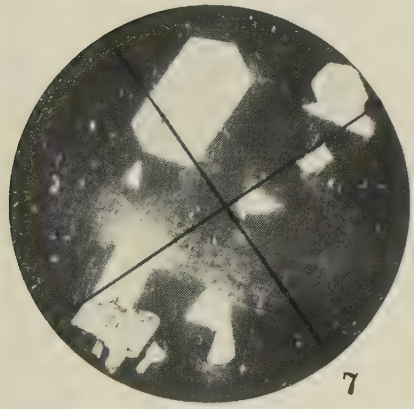
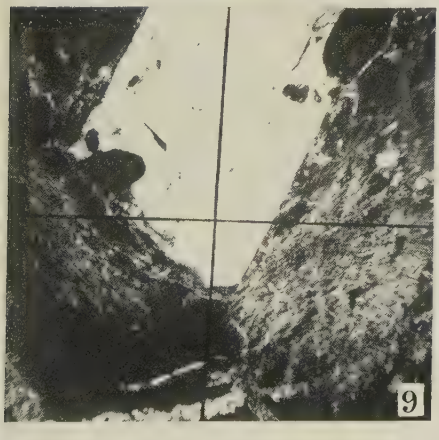
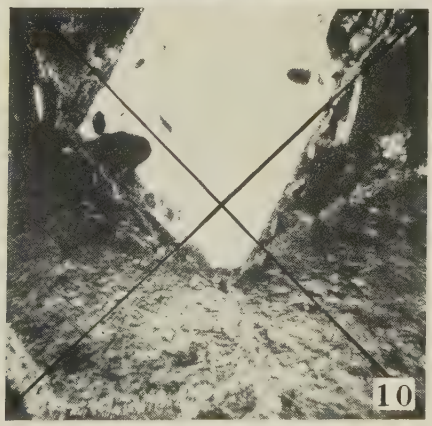
[1] L. Hawkes, On an olivine dacite in the Tertiary volcanic series of eastern Iceland. Quart. Journ. Geol. Soc., 1924, vol. 80, p. 560.









L. Hawkes and H. F. Harwood: Anorthoclase-bearing Rock-glass.

Legrandite, a new zinc arsenate.

By Julien Drugman, Ph.D., M.Sc.
and Max H. Hey,[1] B.A., B.Sc.
With X-ray measurements by F. A. Bannister,[1] M.A.

[Read June 7, 1932.]

AMONG a number of specimens which the senior author (J. Drugman) obtained some years ago from the widow of a mine manager, Mr. Legrand, of Belgian nationality, was one of massive blende from the Flor de Peña mine,[2] Lampazos, Nuevo Leon, Mexico, which carried a small quantity of a bright yellow, transparent substance that could not be identified with any known mineral. Goniometric and optical examination showed it to be monoclinic, but the material was mainly massive radiating-prismatic, and the few freely developed crystals gave only very approximate measurements (see table II). A chemical analysis by the junior author showed it to be indeed a new mineral, a basic zinc arsenate, and the name 'legrandite' is proposed for it in recognition of the collector. The larger part of what remains after investigation of the small specimen has been presented to the British Museum for preservation in the mineral collection.

The results of the chemical analysis are given in table I, and the molecular ratios (column 4) at first suggested the formula $Zn_3As_2O_8.3H_2O$, to which they offer a fair approximation. But the X-ray examination showed that this formula is impossible. The specific gravity[3] (determined by flotation in Clerici solution) is $4{\cdot}01 \pm 0{\cdot}05$, and together with the measured cell-size, this leads to a cell-content of 4·54 molecules of the above formula, which is clearly out of the question. Computing instead the actual atomic cell-contents from the specific gravity, cell-size, and chemical analysis, the figures given in column 5 are obtained; allowing for the fact that the determined

[1] Assistant-Keepers in the Mineral Department of the British Museum of Natural History.

[2] Stated by Mr. Legrand to be a 'mine with complex zinc and lead minerals, unfortunately very rich in arsenic, which renders it unworkable'.

[3] Two determinations were made and gave sp. gr. 3·98 and 4·04.

amount of ferric oxide may include a little arsenic pentoxide, these agree well with the formula $Zn_{14}(AsO_4)_9OH.12H_2O$, which is therefore proposed for the mineral.[1] As columns 2 and 3 of table I show, the composition calculated from this formula agrees distinctly better with the analysis than does the calculated composition for $Zn_3As_2O_8 \cdot 3H_2O$. There is a small degree of replacement of zinc by iron and a trace of manganese.

TABLE I. Chemical analysis and molecular ratios of legrandite; also the atomic cell-contents calculated from the analysis, specific gravity, and X-ray data.

		Calculated for:			
	Analysis.	$Zn_3As_2O_8.3H_2O$.	$Zn_{14}(AsO_4)_9$ $OH.12H_2O$.	Molecular ratios.	Atomic cell-contents.
As_2O_5 ...	42·02 %	43·53 %	43·11 %	1·000	As 8·80
ZnO ...	46·68	46·23	47·49	3·138	Zn 13·79 } 14·45
Fe_2O_3 ...	2·14	—	—	0·073	Fe 0·64 }
MnO ...	0·05	—	—	0·003	Mn 0·02 }
H_2O ...	9·36	10·24	9·40	2·842	H 24·98
Total ...	100·25	100·00	100·00	—	—
Oxygen ...	32·69 %	33·30 %	32·68 %	11·176	O 49·01

Weight of material used for the analysis 0·2190 gram. The arsenic was precipitated as sulphide and weighed as magnesium pyroarsenate. The zinc was precipitated as sulphide and weighed as pyrophosphate. Manganese was determined colorimetrically, and the total iron was estimated as Fe_2O_3. Calcium, magnesium, and cadmium were tested for and found to be absent. Owing to the small amount of material available, the water could only be obtained as loss on ignition; qualitative tests show that carbonates are absent, but fluorine or chlorine might possibly be present and would be included with the water.

The colour of the mineral as observed on the specimen is canary-yellow, but closer examination shows that it is not uniform—in places the mineral is almost, if not quite, colourless. It is possible that the iron shown by the analysis was originally present in the mineral in the ferrous state, and that the yellow colour is due to local oxidation of the iron, corresponding to an isomorphous admixture of $Zn_{13}(AsO_4)_9FeO.12H_2O$ instead of $Zn_{13}(AsO_4)_9FeOH.12H_2O$, but the quantity of material was insufficient to test this point, or to determine the state of oxidation of the iron. The pleochroism mentioned below suggests that the colour, although non-uniform, is not due to inclusions of limonite. Moreover, the crystals were all perfectly clear.

[1] The comparative complexity of the formula as shown by the X-ray data suggests that the simple formulae usually given to some other arsenates and phosphates may require revision.

The refractive indices of the mineral were measured by the immersion method, which gave α 1·675, β 1·690, and γ 1·735 for sodium-light (all $\pm$0·005), and (very approximately) by the prism method on a small, natural prism (110) : (1$\bar{1}$0). Owing to multiple reflections from the prism-faces, the angle of the refracting prism could not be exactly fixed; hence the values found probably give a fairly accurate measure of the birefringence and dispersion, but only

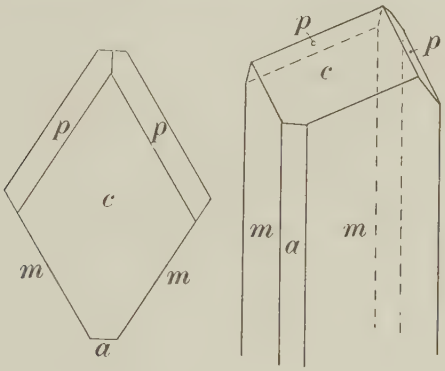


Fig. 1. Crystal of legrandite (plan and clinographic drawing).

a very approximate one of the actual indices. The values found by the prism method were : α 1·702 (red light), 1·709 (yellow), and 1·717 (blue); γ'(vibrations parallel to the *c*-axis) 1·721 (red), 1·724 (yellow), and 1·753 (blue). Approximate determinations of the birefringence, under the microscope, gave $\beta - \alpha$ 0·015 and $\gamma - \alpha$ 0·07. The optical orientation, determined on cleavage fragments under the microscope, is $Bx_o(\alpha) \perp$ b (010), $Bx_a(\gamma)$ at 36 40° to the *c*-axis in the acute angle β. The mineral is optically positive, and the optic axial angle, 2E, was measured approximately under the microscope, and found to be 65° $\pm$ 5°, with $\rho < v$ distinct, and a slight horizontal dispersion of the acute bisectrix. The more deeply coloured parts of the mineral are distinctly pleochroic, the yellow colour of fragments lying on *b* (010) being more intense for vibrations parallel to the acute bisectrix than for those parallel to the third mean line.

An X-ray examination confirmed the monoclinic symmetry of the mineral, and gave the unit-cell dimensions : *a* 12·70, *b* 7·90, *c* 10·18 Å., β = 75° 35′ $\pm$ 5′. The atomic contents of the unit cell are discussed above. Time did not permit of a determination of the space-group,

but a short study of the Lauegram suggests that the lattice is the simple monoclinic. The axial ratio, calculated from the X-ray measurements, is $a : b : c : = 1{\cdot}6075 : 1 : 1{\cdot}2886$, which will be seen to agree reasonably well with the approximate goniometric measurements (table II).

The only crystals suitable for goniometric measurement were three very tiny prisms, 1–2 by 0·1–0·2 mm., found in a cavity; they show the forms $a(100)$, $m(110)$, $c(001)$, and $p(\bar{1}11)$, but all the faces are poorly developed and give multiple reflections, those given by a and m being spread out in the zone [001], those given by c in [010], and those given by p in [110]. On m there are striations at 54° to the c-axis, parallel to the zone-axis $[\bar{1}11]$ (calculated angle $[001] : [\bar{1}11] = 50° 56'$). The goniometric measurements are given in table II, the calculated values being derived from the more accurate X-ray data.

TABLE II. Goniometric measurements of legrandite, with calculated values from the X-ray data. ($a : b : c = 1{\cdot}6075 : 1 : 1{\cdot}2886$; $\beta = 75° 35'$.)

Interfacial angles:	Measured.	Limits and no. of angles.	Calculated.
$am(100) : (110)$ ...	57° 13′	56° 7′–60° 13′ (14)	57° 17′
$ac(100) : (001)$ ...	75 25	71 36 –78 22 (4)	75 35
$mc(110) : (001)$ ...	82 1	81 30 –82 22 (4)	82 16
$pc(\bar{1}11) : (001)$ ...	60 58	59 17 –62 26 (4)	61 25
Interzonal angle:			
$[ca] : [cpm] = [010] : [110]$	57 46	55 18 –60 31 (8)	58 7

The original measurements were made by the senior author on a two-circle goniometer with the zone [001] in zone-adjustment, and have been in part re-computed for convenience of presentation. The setting is in agreement with the conventions suggested by Dr. T. V. Barker (Systematic crystallography, London, 1930), and the classification angles are: $cr(001) : (101) = 32° 54'$, $ar(100) : (101) = 42° 40'$, $am(100) : (110) = 57° 17'$, $bq(010) : (011) = 38° 42'$.

The specimen consists mainly of reddish-brown blende, and carries, besides the legrandite, occasional minute crystals of pyrite, and in numerous minute cavities there are tiny whitish hexagonal crystals, perhaps mimetite, and lenticular crystals resembling chalybite.

The distinction of pyrite from marcasite in nodular growths.

By F. A. Bannister, M.A.
Assistant-Keeper in the Mineral Department of the British Museum of Natural History.

[Read March 15, 1932.]

A RECENT account of pseudo-meteorites by Dr. L. J. Spencer[1] includes a description of nodules of pyrite 'popularly thought to be "thunderbolts"'. Dr. Spencer himself collected in 1931 a large number from the Lower Chalk outcropping on the foreshore below 'The Warren' at Folkestone, Kent. Some of these show well-developed octahedra 5 to 10 mm. across on the outer surface, undoubtedly to be referred to pyrite. More commonly the nodules exhibit small distorted octahedra which might easily be mistaken for marcasite. Indeed, in the past, many of these nodules from the Chalk at Folkestone and elsewhere, have been named marcasite, and they were so labelled in the British Museum collection. Dr. Spencer, therefore, suggested that modern methods should be applied to those cases where the crystalline form is distorted or not sufficiently developed to serve as a means of distinction between pyrite and marcasite. The methods suggested in his paper are (1) X-rays, (2) polarized light reflected from polished sections of nodules.

Before passing to an account of the technique employed and the results obtained by the present investigations, a short review will be given of the methods employed by previous workers in this field. The crystallographic distinction based on the difference in forms exhibited by well-formed crystals of cubic pyrite and orthorhombic marcasite is dealt with adequately in text-books, and need not be dwelt upon here. The following table shows that all observers are agreed that marcasite is lower in density than pyrite (p. 180). If we place most reliance on recent measurements the probable difference in density of the two minerals is over 0·10, but certainly less than

[1] L. J. Spencer, Nat. Hist. Mag. British Museum (Natural History), 1931, vol. 3, p. 56.

0·20. It is clear that density measurements on nodular growths cannot be conclusive, and are quite useless if we are looking for a mixture of the two minerals in the same specimen.

Authority.	Density of Marcasite.	Pyrite.
Dana[1]	4·85—4·90	4·95—5·10
Spencer[2]	4·609–4·887	4·970–5·169
Stokes[3]	4·88—4·90	5·02—5·04
Allen[4]	4·887	5·027
Bannister (X-ray) ...	4·90	5·03

The case for colour distinction has been put very clearly by H. N. Stokes (loc. cit.), and my own observations are in agreement with his conclusions. Text-book descriptions of colour are based in most instances on tarnished specimens. Freshly fractured or polished surfaces of pyrite and marcasite are pale brass-yellow and tin-white respectively; the latter colour is not restricted to arsenical marcasite. The comparison of fresh surfaces in ordinary white light is the most simple test that can be applied. More elaborate methods are only justified in the study of fine-grained intergrowths, or where we suspect the presence of small quantities of pyrite in marcasite, or vice versa.

Chemical methods of distinguishing pyrite from marcasite have been described, but they are not reliable unless the exact conditions of the original experiments are repeated. Surface effects more especially influence the success of such qualitative tests. The studies of Stokes and later those of E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen (loc. cit.), are, however, on a different footing, and the quantitative results obtained merit closer attention. In Stokes's method an excess of finely powdered mineral is boiled with an aqueous solution of a ferric salt in an atmosphere of carbon dioxide. The oxidation is supposed to take place in two stages:

(1) $FeS_2 + Fe_2(SO_4)_3 = 3FeSO_4 + 2S$,
(2) $2S + 6Fe_2(SO_4)_3 + 8H_2O = 12FeSO_4 + 8H_2SO_4$.

It was found that in the case of marcasite about 18 % of the total

[1] E. S. Dana, System of Mineralogy, 6th edition, 1892, pp. 85, 94.
[2] L. J. Spencer, Min. Mag., 1927, vol. 21, pp. 363–364.
[3] H. N. Stokes, Bull. United States Geol. Survey, 1901, no. 186, p. 12.
[4] E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen, Amer. Journ. Sci., 1912, ser. 4, vol. 33, p. 170.

sulphur was oxidized according to the second equation above, whereas 60 % was the figure for pyrite. Apparently these figures are not affected by varying the grain of the material used, and so the difference in the oxidation figures cannot be accounted for by surface differences. Only the speed of the reaction, not the equilibrium state, is affected by the fineness of powdering. Upon these experiments Stokes bases the determination of the amounts of marcasite and pyrite in mixtures of known proportions, and then applies the method to various specimens including nodular growths. He probably claimed too high an accuracy for his results. The later work of Allen, Crenshaw, Johnston, and Larsen, does, however, confirm, with certain exceptions of detail, the main features of the method. Since Stokes's work in 1901 new methods of investigation have arisen, and the results now obtained on specimens similar to those he used should be in complete agreement.

The application of X-ray methods to this type of problem is generally straightforward and some freedom of choice is in this case possible. The powder method though, perhaps, the most obvious method is subject to at least two disadvantages: (1) any orientation of crystalline matter in the original specimen is lost by powdering; (2) the time of exposure is longer than for single crystal photographs. When single crystal fragments, or fibrous or platy aggregates, can be isolated, the rotation method should be employed. Even when a specimen appears to be compact and very fine-grained it is better to use a chip than to powder a fragment for investigation. It was first necessary to take single crystal photographs of known material for comparison, not only for marcasite about the three axes a, b, and c, but also for pyrite about a cube axis. The published data for pyrite comprise W. L. Bragg's original X-ray spectrometer results[1] (pyrite was one of the first minerals to be examined in this classical work), Ewald's Laue photographs,[2] and data from powder photographs of various other authors.[3] The rotation photographs constitute valuable identifications of the minerals and are superior to powder photographs since complete coincidence in the positions and intensities of spots must occur in two dimensions, not merely in one. Rotation photographs

[1] W. L. Bragg, Proc. Roy. Soc. London, Ser. A, 1914, vol. 89, p. 468.

[2] P. P. Ewald, Physikal. Zeits., 1914, vol. 15, p. 299.

[3] M. J. Buerger (Amer. Min., 1931, vol. 16, p. 361) in his work on the structure of marcasite used molybdenum radiation. The indices and intensities of spots on marcasite photographs obtained in the present work using $Cu-K_\alpha$ radiation are in substantial agreement with his data.

of marcasite about the a and b axes are at once distinguishable from a photograph of pyrite about a cube axis, simply by the difference in the spacing of the layer-lines. In a cylindrical camera of

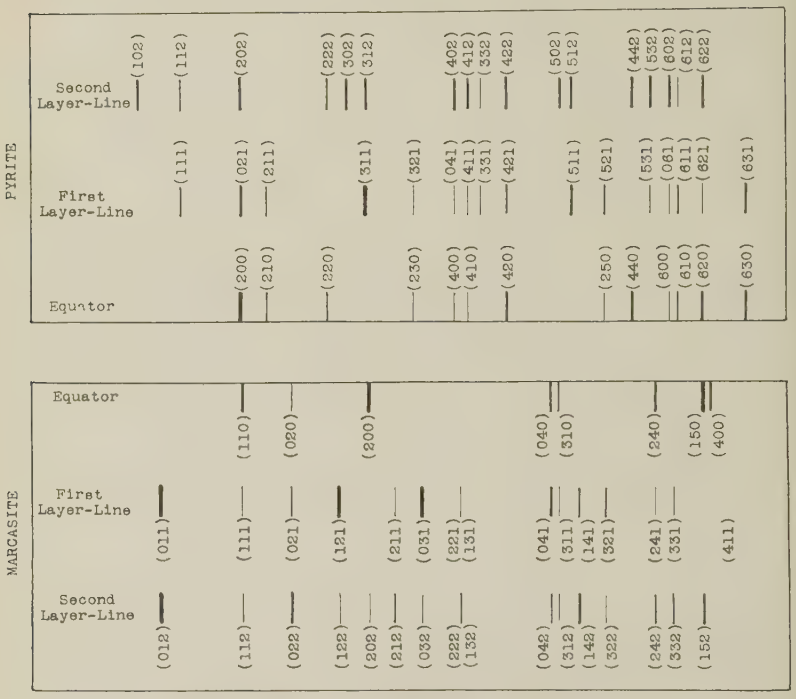


FIG. 1. Diagrams of rotation photographs of pyrite (about a cube axis) and of marcasite (about the c-axis). The width of each diffraction line represents the visually estimated intensity on the original photograph. Camera diameter 6·04 cm.; $Cu - K_\alpha$ radiation, $\lambda = 1{\cdot}539$ Å., using a nickel filter.

diameter 6·04 cm., and using $Cu - K_\alpha$ radiation, the distances $2r$ between the various layer-lines above and below the equator are:

	Distances $2r$.			
	1st layer-line.	2nd layer-line.	3rd layer-line.	Spacing.
Marcasite about [100] ...	3·08 cm.	*	*	3·38 Å.
,, ,, [010] ...	2·23	5·80 cm.	*	4·44
,, ,, [001] ...	1·80	4·20	10·07 cm.	5·39
,, ,, [110] ...	1·77	3·97	8·90	5·58
Pyrite about [100] ...	1·80	4·19	9·96	5·40

* These layer-lines do not fall upon the film.

In order to distinguish photographs of marcasite about the [001] and [110] axes from pyrite [100] photographs, it is necessary to study also the distribution of spots along the layer-lines. This has been done very carefully and fig. 1 shows the rotation diagrams for photographs of marcasite and pyrite about the [001] axis. The layer-line spacing is practically identical and certain spots along the equator

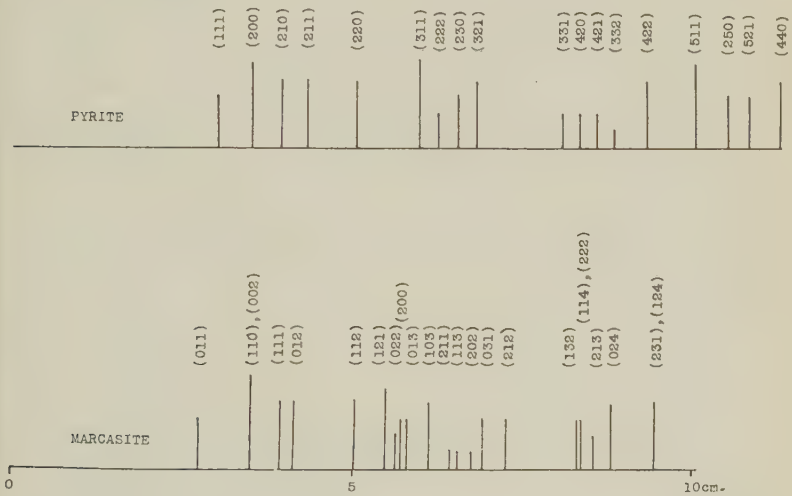


Fig. 2. Diagram of powder photographs of pyrite and marcasite. The heights of the ordinates represent the visually estimated intensities of the lines on the original photographs. Camera diameter 6·04 cm.; $Cu - K_\alpha$ radiation, $\lambda = 1{\cdot}539$ Å., using a nickel filter.

coincide, but the two diagrams are not superposable and are readily distinguished. Although the rotation diagram for marcasite about the [110] axis differs from pyrite a little in its layer-line spacing, the equatorial spots are nearly coincident, and it is only when the first and second layer-lines are compared that striking differences are found. It is generally possible to set a crystal fragment of pyrite or marcasite with a face parallel to the axis of rotation, so that it is highly necessary to have a knowledge of photographs about important zone-axes of the minerals concerned.

Having obtained the rotation photographs and indexed them carefully it is possible to index the powder photograph of marcasite with certainty. Fig. 2 shows a comparison of the powder photographs of pyrite and marcasite. They are reproductions to scale of the

distribution of the lines, and the intensities are represented by the lengths of the ordinates. The important conclusions to be drawn from the comparison are: (1) the number of coincident lines when the two photographs are superposed; (2) the possibility of ensuring freedom of each specimen from its polymorph by considering certain important lines. The powder photographs serve as standards for comparison only when they have been studied in this way. It is best to take these standard powder photographs on large films using a circular aperture as Debye originally did and not a parallel-jawed slit system. If a crystal fragment set in chance orientation be rotated, the resulting photograph cannot always be associated with one of the rotation photographs about a zone-axis. It is always possible to superpose it upon an 'extended' powder photograph of the same substance.

The three X-ray methods employed may thus be summarized:

(1) Rotation photograph of crystal fragment about any important zone-axis.

(2) Rotation photograph of crystal fragment about an axis in chance orientation.

(3) Powder photographs.

The nodules of iron disulphide, so abundant in the Chalk of the south of England, show a considerable variation in shape and size, and all possible gradations between a smooth outer limonitized surface and a surface made up of quite large crystals. If a nodule be broken open the bulk of the material is seen to be made up of compact radiating blade-like aggregates, pale brass-yellow in colour, terminating at the surface in large or small crystal faces. The blades do not, however, generally terminate at the centre; a fine granular material occupies the central space, which varies from a few millimetres to a centimetre in diameter. There is no appearance in any nodule I have examined of concentric layers and the colour of a freshly fractured nodule is always the pale brass-yellow typical of pyrite.

X-ray rotation photographs have been taken of blade aggregates from the interior of several nodules, and also of crystal fragments from the surface. Powder photographs have also been taken of the granular material from the centre. The granular material sometimes contains gypsum crystals which were picked out before taking a photograph. All the nodules from Folkestone, Kent, and Oxted, Surrey (nos. 1, 2, and 3) yield pyrite photographs whichever part of the nodule is tested. Long exposures failed to detect any weak

marcasite lines. The blade aggregates yield photographs which show that the blades are elongated along a cubic axis and flattened parallel to a cube face. Small ellipsoidal nodules showing no internal radial structure from a pebble of calcareous shale collected on the beach at Newhaven, Sussex (no. 4), also proved to be pyrite, and not marcasite as labelled.

The only aggregated specimens of true marcasite examined were the elongated cylindrical stalactites from Mineral Point, Wisconsin, U.S.A. (no. 7). These break perpendicular to the axis of elongation and are radiating structures terminating on the surface in large or small crystals with the form of marcasite. The colour on a fresh surface is tin-white, and crystals from the surface and also fragments from the interior yield marcasite photographs. No pyrite lines could be detected.

The following table summarizes these results :

No.	Locality.	B.M. No.	X-ray result.
1.	Folkestone, Kent	unregistered duplicate	pyrite
2.	ditto	ditto	ditto
3.	Oxted, Surrey	1931,141	pyrite
4.	Newhaven, Sussex	88316	pyrite
5.	Sparta, Illinois, U.S.A. (disk in shale)	84424	pyrite
6.	Bordean chalk pit, Langrish, Petersfield, Hampshire	1910,364	pyrite
7.	Mineral Point, Wisconsin, U.S.A.	35744	marcasite

X-ray methods afford the most certain means of distinction between marcasite and pyrite. Only a small quantity of material, however, can be photographed at any one time. Polished sections of nodules have therefore been examined by reflected polarized light in order to discover any intergrowth of marcasite with pyrite. This second method permits a comparatively rapid survey of an area 1–2 sq. cm., and its success depends upon a ready distinction between marcasite and pyrite. Schneiderhöhn's data[1] show that this should be easily achieved. I used as standards of comparison polished sections of spear-head marcasite twins from the Chalk of Folkestone, and fresh plane surfaces on large pyrite crystals from Morro Velho, Brazil. Between crossed nicols, marcasite shows characteristic and vivid yellow, plum, and pale-green polarization colours. The pyrite crystals are completely isotropic. The trace of the twin-plane (110)

[1] H. Schneiderhöhn and P. Ramdohr, Lehrbuch der Erzmikroskopie, 1931 Berlin, vol. 2, pp. 157, 192; see also coloured plate, no. 2.

in marcasite is a further aid to discrimination. The nodules from the Chalk examined by X-ray methods yield isotropic sections made up of radiating crystals weathered on the surface to limonite, which appears a grey to brown finely grained mineral between crossed nicols.

Further sections of nodules from the Chalk give the same result. In certain cases where weathering has been severe, the limonite appears to reach down in dendritic growths between the blades of pyrite. Not a single nodule from the Chalk so far examined has revealed an intergrowth of marcasite. The true marcasite stalactites from Wisconsin, U.S.A., possess an outer zone of large marcasite crystals showing twinning and therefore giving alternate bands of the polarization colours described above. The inner portion of the stalactite is far more compact than a pyrite nodule and between crossed nicols shows pale yellow and mauve blotches which change colour on rotating the section. The anisotropy is manifest throughout the whole nodule.

A closer examination of two sections of pyrite nodules from the Chalk revealed very weak anisotropy. These sections possessed a higher polish than the others and neighbouring blades showed very faint pink and blue polarization colours which changed on rotating the section. This effect may easily be overlooked, and it is sharply distinguished from the anisotropy of marcasite. Moreover, one of the sections showing this effect had already been examined thoroughly by X-ray methods and shown to be typical pyrite. The polarization colours though very faint can be followed over the whole section so that it cannot be attributed to any local effect or inclusion. It is a property of the nodule as a whole. Several writers have referred to anisotropic pyrite and Schneiderhöhn states that it can always be distinguished from true marcasite. He attributes the anisotropy in certain cases to arsenic content. Ehrenberg[1] claims that powder photographs of banded pyrite from Aachen show small differences in the positions of the lines from those of a normal pyrite photograph, and he attributes this to the excess of iron found by chemical analysis. His polished sections, however, are isotropic. Any replacement of sulphur by arsenic atoms in the pyrite structure would affect the intensities of diffracted spots on a rotation photograph. Ehrenberg does not give any X-ray data to support his contention that additional iron atoms are present in the structure of the Aachen pyrite. Any such addition would certainly reveal itself more clearly in changes

[1] H. Ehrenberg, Neues Jahrb. Min., Abt. A, 1928, vol. 57, p. 1303.

of intensity than cell-size. The X-ray rotation photographs of blades from the anisotropic nodules of pyrite from the Chalk at Folkestone appear to be normal in intensity and in the positions of the spots. There is no X-ray evidence of departure from the normal pyrite structure. I would attribute the anisotropy of these nodules to a condition of strain. The final appeal in any doubtful case that may arise should be to X-ray methods.

It is now necessary to see how the present results agree with Stokes's work. The later work of Allen, Crenshaw, Johnston, and Larsen shows that the determination of any one component in a mixture of pyrite and marcasite is accurate to $\pm 5\%$ and probably less accurate for mixtures near to pure pyrite or marcasite. Stokes examined one nodule, 'No. 25', from Folkestone, Kent, evidently similar to those studied in the present work, in which he found 3% of marcasite, but this result must be regarded as very doubtful. He also states 'I have received several supposed marcasite concretions from Folkestone all of which are clearly pyrite'. Some specimens he examined were undoubtedly mixtures, and contained about 30% pyrite; but these were not nodular growths, and a fractured surface revealed the two minerals by colour difference. Intergrowths of pyrite and marcasite have been recorded by other writers. Interesting cases, in particular, are those of parallel growths of marcasite twins on cubes of pyrite cited by Sadebeck[1] and Trechmann.[2] The spear-head marcasite twins from Folkestone, Kent, show warty excrescences of pyrite and in some cases a regular parallel growth of pyrite cubes, the cube axes being arranged parallel to the twin-plane (110). In these cases, parallel growth occurs when the [001] and the [110] axes of marcasite are coincident with the cube axes of pyrite, the spacings being 5·39, 5·58, 5·40 Å. respectively. These examples of intergrowth are quite obvious from an examination of the crystal forms and colour. The nodules from the Chalk, however, are from all methods definitely pyrite and no case has yet been found among them of intimate intergrowth of the two minerals.

In conclusion I should like to thank Dr. W. R. Jones of the Imperial College of Science and Technology who has assisted me personally throughout the course of the metallographic work and who placed additional sections, made under his supervision, at my disposal.

[1] A. Sadebeck, Ann. Chem. Phys. (Poggendorff), 1878, Erg.-band 8, p. 625.
[2] C. O. Trechmann, Min. Mag., 1892, vol. 9, p. 209.

Determination of minerals in platinum concentrates from the Transvaal by X-ray methods.

(With Plates VII and VIII.)

By F. A. Bannister, M.A.

With chemical analyses and syntheses by M. H. Hey, B.A., B.Sc.

Assistant-Keepers in the Mineral Department of the British Museum of Natural History.

[Read June 7, 1932.]

CONCENTRATES from the platiniferous norites of the Bushveld, Transvaal, are not completely soluble in aqua regia. The insoluble portion consists of steel-grey fragments first analysed chemically by R. A. Cooper [1] and considered by him to be a new platinum mineral represented by the formula $Pt(As,S)_2$. The name cooperite was proposed for the new mineral by F. Wartenweiller,[2] and after further work Cooper decided that the arsenic found in the early analysis was due to the presence of sperrylite, and he changed the formula [3] to PtS_2. H. Schneiderhöhn [4] observed simple twinning and, less frequently, polysynthetic lamellae on polished sections of mineral grains from the same deposits, and he suggested that cooperite is probably orthorhombic and isomorphous with marcasite. The latest account of the new mineral has been published by H. R. Adam [5] who gave several analyses of cooperite from the Rustenburg and Potgietersrust districts and concluded that the 'mineral is PtS_2 with a

[1] R. A. Cooper, Journ. Metall. Mining Soc. South Africa, 1928, vol. 28, p. 281. [Min. Abstr., 4–10.]

[2] In the discussion on Cooper's paper. See also Min. Mag., 1931, vol. 21, p. 618.

[3] R. A. Cooper, Journ. Metall. Mining Soc. South Africa, 1929, vol. 29, p. 230 (final discussion to the preceding paper).

[4] H. Schneiderhöhn, Centr. Min., Abt. A, 1929, p. 193. [M.A. 4–149.] H. Schneiderhöhn and P. Ramdohr, Lehrbuch der Erzmikroskopie, Berlin, 1931, vol. 2, p. 216.

[5] H. R. Adam, Trans. Geol. Soc. South Africa, 1931, vol. 33 (for 1930), p. 103. [M.A. 4–500.] See also discussion in Proc. Geol. Soc. South Africa, 1932, Trans. vol. 34 (for 1931), pp. xxxv and xlii.

small amount of excess metal (platinum, palladium, and nickel) present in solid solution'. G. V. White in the same paper figured a 1 mm. crystal picked out from fragments of cooperite from Potgietersrust, Transvaal. Perhaps influenced by Schneiderhöhn's results, White wrongly interpreted his accurate goniometric measurements as conforming with orthorhombic symmetry. In the abstract of this paper it was pointed out by L. J. Spencer that the crystal is 'clearly pyritohedral-cubic with the forms (100), (111), (210), and elongated along a cubic axis'. This crystal and a number of small fragments were then sent to Dr. Spencer for further investigation. At his suggestion X-ray methods have been applied and it has been possible by their aid alone to distinguish three different minerals amongst the fragments originally analysed and called cooperite. Moreover, through the kindness of Mr. H. R. Adam, who sent further supplies both of the cubic crystals and the cooperite fragments, sufficient quantities of each of the three minerals have been separated by X-ray methods to carry out more or less satisfactory chemical analyses. In addition to these three minerals the concentrates also contain flattened cubes of magnetic (iron-bearing) platinum, some sperrylite, and possibly two as yet undetermined minerals.

Cooperite.

Rotation and Laue photographs of the crystal no. 1 figured by White confirmed conclusively its cubic symmetry and also gave evidence that its structure must be of the pyrite type (pl. VII, fig. 4). A powder photograph of a few of the cooperite fragments from Rustenburg, however, cannot be interpreted on this basis. It is obvious that the lines to be expected for the cubic material or for sperrylite are not present. Most of the cooperite fragments are irregular flakes each weighing from 0·1 to 0·2 mg., but one elongated crystal no. 2 was picked out showing four good prism-faces. Neither the angles of the prominent prism-zone ([101], see p. 193) nor a rotation photograph parallel to the direction of elongation are compatible with cubic symmetry. The diffraction spots of this rotation photograph are, however, all superposable upon lines present on the powder photograph already mentioned, and all the prominent lines on the powder photograph can be accounted for in this way. This proves that crystal no. 2 represents the principal component present amongst the cooperite fragments. A complete X-ray study of this crystal was therefore proceeded with. A series of Laue and rotation

photographs shows that it possesses tetragonal symmetry (pl. VII, fig. 3). Having deduced the dimensions of the unit cell and indexed the rotation photographs it was possible to assign indices to all the prominent lines of the powder photograph. A few weak lines remained indicating the presence of at least one other mineral.

Further cooperite fragments were then selected and a rotation photograph taken of each one in succession. The photographs were taken in random orientation (pl. VIII, fig. 8), and the identity of a particular fragment with that of crystal no. 2 was proved if all the spots of its photograph were superposable upon the indexed lines of the powder photograph (fig. 7). For such work it is necessary to use a powder photograph taken with a pin-hole collimator and, of course, the same diameter camera with a wider film than usual. Seventeen fragments of so-called cooperite from the Rustenburg district were examined in succession by this method and fourteen shown to be identical with crystal no. 2 of the tetragonal mineral. The remaining three were found to be single crystals of a second tetragonal mineral (braggite, p. 198) with different cell-sides from the first. A powder photograph of Cooper's original material from the same locality also showed the presence of these two components in about the same proportions as in the last sample.

The fourteen fragments identical with crystal no. 2 weighed, together, 2·18 milligrams. A partial chemical analysis was carried out upon this material (table I). The metal remaining after chlorination was identified as platinum by microchemical tests. Further, one of the small metal blebs was rotated in an X-ray beam, and the powder photograph obtained was identical with one of finely divided platinum made for comparison. The sulphur content is closer to the figure for PtS than for PtS_2. The second consignment of cooperite from Potgietersrust contains much larger fragments. Four of them, weighing 8·28 milligrams, were selected by X-ray rotation photographs and the results of the chemical analysis are shown in table I. A separate analysis was made upon a further quantity of 5 milligrams to obtain the palladium content. This was found to be less than 3 %. Mr. H. R. Adam has kindly allowed me to print some new analyses[1] he has obtained on grains separated by colour difference under high-power magnification. A. B. Coussmaker[2] has found that the Rustenburg concentrates contain two components which exhibit

[1] Communicated in a letter.

[2] H. R. Adam, loc. cit., Proc., p. xxxv.

different colours on roasting in air. Adam has confirmed this result for material from Potgietersrust and, moreover, finds that the two components show a colour difference under high-power magnification before heating. By weighing each fragment before and after roasting he checks his preliminary colour separation and also discovers any associated sperrylite. Analyses III and IV of table I were carried out upon material separated in this way and provisionally labelled ' cooperite B '. In the meantime Mr. Hey had prepared a number of synthetic platinum sulphides by various methods and two of them gave powder photographs (pl. VIII, fig. 7) identical with those of the

TABLE I. Chemical analyses of cooperite and synthetic PtS and PtS_2.

No.	Pt.	Pd.	Ru, Ir, &c.	Ni.	S.	Total.	Density Observed.*	Density X-ray.
I.	[83·0]†	—	—	—	17·5‡	100·0	—	—
II.	[85·6]	trace	—	0·1	14·3‡	100·0	9·5	10·2
III.	82·2	2·6	—	trace	14·4	99·2	—	—
IV.	80·26	4·31	0·62	trace	14·36	99·55	—	—
V.	[82·7]	—	—	—	17·3	100·0	9·0	10·1
VI.	[84·6]	—	—	—	15·4	100·0	—	10·1
VII.	85·9	—	—	—	14·1	—	—	10·1
VIII.	[75·3]	—	—	—	24·7	100·0	7·2	7·86

I. Cooperite (2·18 mg.) from Rustenburg, Transvaal; analysed by M. H. Hey. Unit-cell edges $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å.

II. Cooperite (8·28 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey. Unit-cell edges $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å.

III. 'Cooperite B' from Potgietersrust, Transvaal; analysed by H. R. Adam.

IV. 'Cooperite B' from Potgietersrust, Transvaal; analysed by H. R. Adam.

V. Synthetic PtS (M. H. Hey); $a = 4{\cdot}92$, $c = 6{\cdot}12$ Å.

VI. Synthetic PtS (M. H. Hey); $a = 4{\cdot}92$, $c = 6{\cdot}12$ Å.

VII. Theoretical figures for PtS.

VIII. Synthetic PtS_2 (M. H. Hey); $a = 3{\cdot}54$, $c = 5{\cdot}02$ Å.

* The observed densities were obtained by the pyknometer method and are correct only to one or two units owing to the small amounts of material used.

† The figures in brackets are those obtained by difference.

‡ The sulphur content in these two cases was obtained by precipitation as $BaSO_4$. In the remaining analyses the figure given is for the loss of weight on ignition. The loss of weight on ignition for analysis II was also 14·3 %.

tetragonal component under discussion. Analyses of these powders are given, together with the calculated figures for PtS. Two other preparations of synthetic platinum sulphide proved to be hexagonal PtS_2 and identical with the PtS_2 prepared by Thomassen.[1] The data for one of these preparations are given in table I for comparison.

[1] L. Thomassen, Zeits. Physikal. Chem., Abt. B, 1929, vol. 2, p. 349.

W. Biltz and R. Juza [1] have also synthesized both platinum sulphides and given densities of 10·09 and 10·04 for two preparations of PtS, and 7·67 and 7·65 for two preparations of PtS_2. One of Mr. Hey's PtS preparations (analysis V, table I), contains a few small hexagonal flakes. A rotation photograph of a single flake identified it as hexagonal PtS_2, and faint PtS_2 lines were also observed on the powder photograph of this preparation. This presence of a small quantity of PtS_2 accounts for the high sulphur content and low density observed. It may be added that no hexagonal PtS_2 has been detected in the Transvaal concentrates. This compound has a perfect basal cleavage and it would probably be lost in the process of washing the concentrates.

The X-ray data show convincingly that the predominant tetragonal component of the so-called cooperite fragments both from Potgietersrust and Rustenburg is PtS, the material from the former locality only differing from the synthetic compound by a small palladium and nickel content. I propose, therefore, that the name cooperite be retained for this component, its ideal composition being PtS, not PtS_2.

It is possible now to combine the X-ray data obtained on cooperite crystal no. 2 with the chemical results and deduce the axial ratio, cell contents, and probable structure of this simple mineral. The approximate density and chemical analysis are consistent with a content of 4PtS per unit cell; the cell dimensions deduced from the X-ray photographs of crystal no. 2 being $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å., $c/a = 1{\cdot}242$. All spots corresponding to indices (hkl) for $(h+k)$ odd, are missing, showing that a tetragonal cell has been chosen with the square end faces centred. In addition, all indices of the type $(0kl)$ for $(k+l)$ odd, and, of course, $(h0l)$ for $(h+l)$ odd, are absent. The only three space-groups consistent with these halvings are D^2_{2d}, C^7_{4v}, and D^9_{4h}. Assuming holohedral symmetry, the most probable space-group is D^9_{4h}. An optional setting of the unit cell with $a = 4{\cdot}91/\sqrt{2}$, $= 3{\cdot}47$, $c = 6{\cdot}10$ Å. is possible, but the face-centred setting has been retained because the probable structure of cooperite can be regarded as built up from expanded face-centred unit cells of platinum.

Having chosen a setting for the unit cell and therefore the axial ratio $a : c = 1 : 1{\cdot}242$, it is possible to assign consistent indices to the forms developed upon the crystal fragments of cooperite (PtS). The

[1] W. Biltz and R. Juza, Zeits. Anorg. Chem., 1930, vol. 190, p. 168.

only fragment so far separated showing definite faces is crystal no. 2 already studied in detail by X-ray methods. The fragment measuring $1{\cdot}0 \times 0{\cdot}26 \times 0{\cdot}26$ mm. is elongated parallel to [101]. The four elongated faces in this zone are of the form (111); the other four faces of the form being very small. In addition, the forms (110) and (001) are present as small faces, but the form (100) cannot be observed. Success in noting the small faces and measuring the interfacial angles was due to setting the crystal with the axes [100], [110], and [001] vertical in succession by X-ray methods. The angles measured were $(110) : (1\bar{1}0) = 90° 5'$, $(111) : (\bar{1}11) = 76°$, and $(001) : (111) = 60° 18'$. The values of the latter two angles calculated from the X-ray axial ratio should be 75° 50′ and 60° 21′ respectively. The images of the faces (111) in the zone [101] are bright but very diffuse; the probable error of measurement is $\frac{1}{4}$ degree; hence the discrepancy between the measured and calculated values of the angle $(111) : (\bar{1}11)$. Crystal fragments of cooperite from Potgietersrust frequently exhibit a cleavage parallel to (111), and they sometimes show distinctly rounded faces.

A probable structure for cooperite will now be proposed consistent with the intensities of the spots observed on rotation photographs. If a crystal of cooperite be rotated about the axis [101] the odd layer-lines are weak, that is, all spots with indices of the type (hkl) where $(k+l)$ is odd, are weak. Thus the vertical faces (100) and (010) of the tetragonal cell are nearly centred. The atomic numbers of platinum and sulphur are 78 and 16 respectively. There is, therefore, strong evidence that the platinum atoms are arranged at the corners and face centres of the tetragonal cell. Of the six possible fourfold positions for platinum in the space-group D_{4h}^{9} only two lead to face-centred grouping. If either of these positions for platinum be associated with each of the five possible fourfold positions for sulphur in turn, only three different structures result. One of the three is a face-centred structure for sulphur as well as platinum. Since a number of spots corresponding to planes with mixed indices are observed on rotation photographs of cooperite this structure is excluded. A decision between the two remaining possibilities is afforded by the small differences between the intensities of certain strong spots (see below). The probable positions of the platinum and sulphur atoms are therefore:

Pt	...	...	$\frac{1}{4}\frac{1}{4}0$; $\frac{3}{4}\frac{3}{4}0$; $\frac{1}{4}\frac{3}{4}\frac{1}{2}$; $\frac{3}{4}\frac{1}{4}\frac{1}{2}$.
S	...	...	$00\frac{1}{4}$; $00\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{3}{4}$.

These positions have been derived from the arrangements (*c*) and (*e*) of Wyckoff's tables[1] where equivalent twofold positions for the simple, not the face-centred, cell are given.

Using these parameters it can be shown that:

I. For planes with all indices odd the structure factor is twice the atomic number of platinum, viz. $F = 156$. All observed spots with these indices are strong and, for a small range of spacing, equal in intensity.

II. For planes with mixed indices: (*a*) l odd, $F = 0$; (*b*) l even, F is twice the atomic number of sulphur, $F = 32$. All observed spots with these indices are very weak.

III. For planes with all indices even: (*a*) $(h+k+l)/2$ even: $F = 156+32 = 188$; (*b*) $(h+k+l)/2$ odd, $F = 156-32 = 124$.

	Structure factor F.	Indices of strong spots.								
III (*a*)	188	(202)	(220)	(224)	(004)	(400)	(404)	(422)	(206)	(440)
III (*b*)	124	(002)	(200)	(222)	(204)	(420)	(424)	(402)	(006)	(600)

All spots with indices in the top row have slightly greater intensities than those below, comparison being made, however, between spots of nearly the same spacing.

The alternative structure of cooperite would only differ in the indices of spots corresponding to structure factors given under III (*a*) and III (*b*) above. All planes with even indices and $(h+k)/2$ even would have a structure factor $F = 188$, and those planes with $(h+k)/2$ odd would have $F = 124$. Thus (002) should be stronger than (202), (402) than (206), &c., which is the reverse of what is actually observed. The intensity data decide against this alternative structure, which, in any case, is improbable, since the sulphur atoms would approach each other too closely.

The proposed structure is made up of planar groups of four sulphur atoms about each platinum atom, and tetrahedral groupings of platinum around sulphur. These groups are so linked that the sulphur atoms of the PtS_4 groups are arranged at the corners of a rectangle, almost a square, the sides being 3·05 Å. or half the cell-height, and 3·47 Å. or cell-side divided by $\sqrt{2}$. The smaller angle subtended at a platinum atom by two sulphur atoms is 82° 36′ and the Pt–S distance is 2·32 Å. The nearest S–S distance is 3·05 Å., and the nearest approach of the platinum atoms is 3·47 Å. The tetrahedral groups of platinum about sulphur are slightly flattened, so that although the Pt–S distance is the same for all four sulphur atoms the angle for a regular tetrahedron 109° 28′ is modified to angles of 128° 20′ and 97° 22′. The structure gives the appearance of a compromise between the almost square PtS_4 groups and the nearly regular tetrahedral SPt_4 groups. If the sulphur atom were moved

[1] R. W. G. Wyckoff, The analytical expression of the results of the theory of space-groups. Washington, 1922, p. 94.

within its tetrahedron of platinum towards the apex, until the tetrahedron became truly regular, the linked sulphur atoms of a PtS_4 group would be pulled out still farther from a true square, and vice versa. Fig. 1 shows the structure drawn to scale; the tetrahedral grouping of platinum about sulphur is clearly shown and also the good cleavage direction parallel to (111). Fig. 2 is a projection of the platinum and sulphur atoms upon the plane (110) and shows the

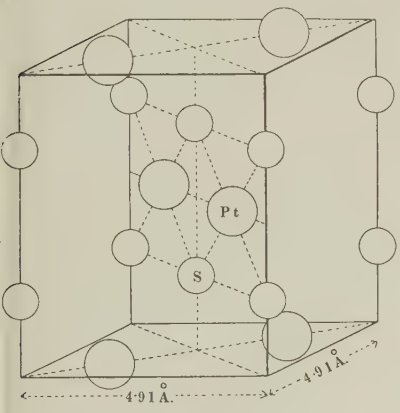


Fig. 1.

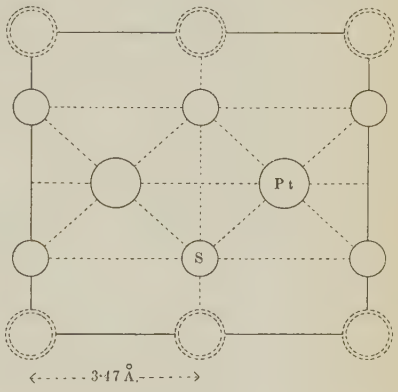


Fig. 2.

Fig. 1. Structure of cooperite. Large circles platinum, small circles sulphur.
Fig. 2. Projection of cooperite structure on the plane (110). Large circles platinum, small circles sulphur. Dotted circles represent platinum 1·735 Å. above and below the (110) plane.

PtS_4 groups. Pauling [1] has shown theoretically that platinum, palladium, and nickel with fourfold co-ordination should form planar MX_4 groups. This prediction has been verified for anions [2] and cations [3] of various complex salts; cooperite is the first binary compound also shown to possess a structure in accordance with Pauling's principle.

Laurite.

The work so far carried out upon the cubic crystal no. 1 (p. 189) figured by G. V. White has distinguished it from cooperite and sperrylite. Rotation and Laue photographs show that its cell-edge is 5·59 Å. and its space group T_h^6: therefore its formula is probably of the type

[1] L. Pauling, Journ. Amer. Chem. Soc., 1931, vol. 53, p. 1367.
[2] S. Sugden, Journ. Chem. Soc. London, 1932, p. 246.
[3] E. G. Cox, Journ. Chem. Soc. London, 1932, p. 1912.

AX_2. An X-ray examination of five further crystals (pl. VII, fig. 4), also from Potgietersrust, showed that they are all identical with the cubic crystal no. 1, and with one exception show the same development of forms and habit. They exhibit in order of importance (100), (210), and (111), faces of the last form being usually small. The crystals show also some variation in the relative development of the cube (100) and the pyritohedron (210), and they are elongated parallel to a cubic axis. The one exception is an elongated crystal of almost scalenohedral habit. Its identity with the others has been proved by rotation photographs about [100], and its axis of elongation, which proves to be [111]. All three usual forms are developed on this crystal but the cube faces have almost vanished. The pyritohedron faces are large and curved, while the octahedron faces are smaller and are truly plane. This crystal actually yields better angular measurements than the others. The average value obtained for (210) : (102) was 66° 24′ and for (210) : (100) 26° 36′ (theoretical values 66° 25¼′ and 26° 34′ respectively). Vicinal faces are often developed, particularly on crystal no. 1. In setting up this crystal for X-ray photographs it was found that the curvature of the two large faces (100) is due to vicinal faces, these being developed on one face about the zone [001], and on the other face about the zone [110].

The composition of the cubic crystals was obtained by a combination of physical and chemical methods. The crystals range in weight from 1½ to 2½ mg. and are, with one exception, rather smaller than crystal no. 1, which measures $1{\cdot}0 \times 0{\cdot}5 \times 0{\cdot}38$ mm. Approximate values of the densities of those crystals nearly rectangular in outline were calculated from the dimensions and weight. Values varying from 5·5 to 6·6 were obtained. Also a pyknometer determination of the density was made upon five crystals (9 mg.). The value 6 so obtained is subject to an error of one to two units. Indeed, the difficulties of the present work on all three minerals have been increased by lack of reliable density data. Available methods do not yield accurate values for small quantities of heavy minerals. The approximate data do, however, show that the cubic mineral has a density of the order of 6 rather than 10. This, in itself, is sufficient to throw doubt upon the metal being one of the three, osmium, iridium, or platinum ; their sulphides if isomorphous with pyrite would all possess densities of the order of 10. A preliminary partial analysis carried out upon one crystal weighing 2·27 milligrams showed that the mineral is a disulphide. Neither platinum nor palladium could

be detected, but there was some evidence for the presence of ruthenium. Microchemical tests for ruthenium are difficult, and it was decided to confirm its presence by X-ray methods. The metallic residue left over from the crystal analysed was applied to the surface of the anode of the X-ray tube. The amount available was so small, however, that the diffractions obtained from calcite were very weak, although they correspond in position to ruthenium K_α and K_β. The second partial analysis of another crystal is given under I in table II. This crystal was roasted in air at a red-heat and then a rotation photograph taken. The powder photograph obtained could be indexed on the basis of a tetragonal cell $a = 4{\cdot}51$, $c = 3{\cdot}11$ Å., agreeing with the dimensions of the cell of synthetic ruthenium dioxide prepared and studied by Zachariasen (pl. VII, fig. 5).[1] The oxide-coated crystal was then reduced in a current of hydrogen and the powder photograph obtained of the metal yielded measurements in exact agreement with the dimensions of the unit cell of ruthenium (pl. VII, fig. 6). Incidentally, this powder photograph reveals no trace of a cubic component of Group VIII and in itself reduces the six possibilities for the composition of the cubic mineral to two, RuS_2 or

Table II. Chemical analyses of laurite.

			Density	
Ru.	Os.	S.	Observed.	X-ray.
I. [67]	—	33	6	6·23
II. 65·2	[3·0]	31·8	6·99	6·23
III. 61·1	—	38·9	—	—

I. Crystal of laurite (1·78 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey. Unit-cell edge $a = 5{\cdot}59 \pm 0{\cdot}01$ Å. The ruthenium content was obtained by difference.

II. Crystals of laurite from gravel deposits, Borneo; analysed by F. Wöhler, Nachr. Gesell. Göttingen, 1866, p. 155; 1869, p. 327.

III. Theoretical values for RuS_2.

OsS_2. Osmium may be dismissed on the evidence of too low density and certainty of formation of OsO_4, at a red-heat when the crystal was roasted in air. Finally, microchemical tests on the metal showed the presence of ruthenium, but osmium could not be detected. The cubic crystals, insoluble in aqua regia, are therefore laurite, RuS_2, a mineral already known in the gravel deposits of Borneo. A sample of laurite sand mixed with platinum, gold, &c., from Pontijn,

[1] V. M. Goldschmidt, Skrifter Norske Videnskaps-Akad. I. Mat.-Naturv. Klasse, Oslo, 1926, no. 1, p. 9.

Tanah-Laut, Borneo, in the British Museum collection (B.M. 40504), was examined and found to contain small rounded crystals with the forms (110), (210), and (111); whilst a rotation photograph about a [110] axis gave $a = 5{\cdot}59 \pm 0{\cdot}01$ Å., confirming its identity with laurite from Potgietersrust. An X-ray study of synthetic RuS_2 has been made by two authors [1] and the structure is the well-known pyrite structure. The present work confirms that the natural mineral is identical with the synthetic compound. A careful study of Laue photographs of pyrite, sperrylite, and laurite has also been made, following Ewald's method,[2] and has shown that the parameter u for all three minerals is close to 0·39. For laurite from the Transvaal u lies between 0·39 and 0·395. The shortest Ru–S distance, assuming $u = 0{\cdot}39$, is 2·35 Å.

Braggite.

The discovery of a third mineral, also tetragonal, but distinct from cooperite, was made when separating, by X-ray methods, the fragments of cooperite for chemical analysis (p. 190). The first crystal of this mineral was found amongst Cooper's original material from Rustenburg. Rotation photographs yielded a unit cell with sides $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å. The crystal, though less than $\frac{1}{2}$ milligram in weight, gives four good prism reflections at 90° intervals. Two larger crystals have also been received from Potgietersrust. These were associated with sperrylite crystals, but X-ray rotation photographs distinguished them readily (pl. VIII, fig. 9). These crystals are both tetragonal prisms, but the pyramidal planes are rounded and quite unsuitable for goniometric measurement. The prism-zone on each crystal yields values differing from 90° at the most by four minutes. The dimensions, weights, and rough density values calculated therefrom are given below:

Locality.	Dimensions.	Weight.	Density.
Potgietersrust ...	1·135 × 0·50 × 0·44 mm.	2·6 mg.	10·5
Potgietersrust ...	1·30 × 0·60 × 0·50	3·0	7·7

Four further fragments of this component were picked out by X-ray methods from Potgietersrust material also containing cooperite. The analysis carried out by Mr. Hey is given in table III. Below this, in the same table, an analysis of presumably identical material by H. R.

[1] W. F. de Jong and A. Hoog, Rec. Trav. Chim. Pays-Bas, 1927, vol. 46, p. 173. I. Oftedal, Zeits. Physikal. Chem., 1928, vol. 135, p. 291.

[2] P. P. Ewald and W. Friedrich, Ann. Physik, Leipzig, 1914, vol. 44, p. 1183.

Adam is reproduced.[1] This material he separated by colour difference under a high-power magnification, and he called it 'cooperite Y' (see p. 191). Both analyses show that the mineral is a sulphide of platinum and palladium containing 3 % to 5 % nickel. The number of sulphur atoms per unit cell is given by $[(x/32)d.a^2c]/1{\cdot}65$, where x is the sulphur percentage directly obtained from chemical analysis, d is the density, a and c are the cell sides given above, and 1·65 is the factor corresponding to the mass of a hydrogen atom. An accurate density value was unobtainable. The average of the values given on p. 198 and the pyknometer value of table III was used. Thence the numbers of sulphur atoms per unit cell calculated for analyses I and II of table III are 8·63 and 7·63 respectively. We may assume that the unit cell of this tetragonal mineral contains eight sulphur atoms. The calculated values depart from the ideal figure owing to errors in the density and sulphur determinations. It can be seen (table III) that the sum of the atomic ratios of the metals approximately equals the atomic ratio of sulphur.

Table III. Chemical analyses of braggite and synthetic PdS.

		Pt	Pd.	Ni.	S.	Density Observed.	Density X-ray.
I.	Per cent.	[58·2]	18·1	4·7	19·0*	10	8·9
	Atomic ratios	0·298	0·170	0·080	0·593		
	Atoms per unit cell ...	4·35	2·48	1·17	8·63		
II.	Per cent.	59·1	20·87	2·8	16·8	—	—
	Atomic ratios	0·303	0·196	0·048	0·524		
	Atoms per unit cell ...	4·42	2·86	0·72	7·63		
III.	Per cent.	—	[80·2]	—	19·8	—	6·87
IV.	Per cent.	—	76·9	—	23·1	—	—

I. Crystals of braggite (10·28 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey; platinum content by difference. Unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å.

II. 'Cooperite Y', from Potgietersrust, Transvaal; analysed by H. R. Adam; also Rh, Ir, &c., 0·42, total 99·99.

III. Synthetic PdS (M. H. Hey). Unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å.

IV. Theoretical values for PdS.

* Sulphur precipitated as $BaSO_4$.

The total number of platinum, palladium, and nickel atoms, therefore, also equals eight per unit cell. The ratio of Pt : Pd : Ni is roughly 4·5 : 2·5 : 1·0. No simple chemical formula that is consistent with the size of the unit cell can, therefore, be given to this mineral. The formula suggested by Coussmaker for the complex polysulphide

[1] Communicated in a letter.

existing in the Rustenburg deposits is 2PtS.2PdS.NiS;[1] but it is possible that he analysed a mixture or perhaps a mineral identical with one of the two unidentified minerals that I have separated from the Rustenburg concentrates (p. 189). It must be emphasized that in dealing with a mixture of opaque minerals reliable chemical data on the several components can only be obtained by analysing grains which have been separated and proved to be identical with each other by other methods.

This being the first new mineral to be isolated and determined by X-ray methods, it may very appropriately be named braggite in honour of Sir William H. Bragg and his son Prof. W. L. Bragg, the pioneers of the new method for the investigation of crystals.

The cell-dimensions of all the crystals and fragments of braggite so far examined are identical. Oscillation photographs have been taken around the axis [100]. The planes (001), (003), (005), and (007) are absent, otherwise there are no systematic halvings. A Laue picture along the *c*-axis also shows marked differences in intensities of the (*hkl*) and (*khl*) spots. Hence the space-group is C_{4h}^2 or C_4^3. The intensities of spots observed on the rotation photographs are not consistent with an approximately face-centred or body-centred lattice for the metal atoms. It is hoped to establish the structure of braggite shortly.

An attempt has been made to synthesize braggite from equimolecular proportions of platinum, palladium, and sulphur. Four preliminary preparations of palladium sulphide containing no platinum all yielded the same powder photographs. Moreover, no obvious relationship with PtS could be detected, the photographs being much more complicated. It was surprising to find, however, that the powder photograph of palladium sulphides is identical with that of powdered braggite (pl. VIII, fig. 10), and the relative intensities of the lines are the same for both. An analysis of one of these sulphides in table III yields the formula PdS, and approximate density values show that the tetragonal unit cell, with practically the same sides as braggite, contains 8PdS. It is probable, then, that braggite and synthetic PdS are isomorphous and that considerable replacement of the palladium by platinum and nickel can occur without disturbing the structure. Braggite may therefore be represented by the formula (Pt,Pd,Ni)S, the palladium and nickel contents being respectively about 20 % and 5 %. It has been noted that cooperite

[1] H. R. Adam, loc. cit., Proc., p. xxxv.

uniform in intensity and no indication of orientation of the particles forming the plate is apparent. There is, however, a definite decrease in the spacing $a = 3{\cdot}87$ Å. For comparison, a powder photograph of finely divided platinum obtained by ignition of ammonium chloroplatinate was obtained which showed exactly the same lines as the photograph of the dull platinum plate and the same relative intensities. The spacing of platinum obtained by ignition is $a = 3{\cdot}93$ Å., and no lines could be detected corresponding to mixed indices.

In conclusion I should like to thank Dr. Spencer for his advice and encouragement during the course of the work. I am also indebted to Mr. Bernal for helpful suggestions on the structure of cooperite.

Summary.—X-ray rotation photographs have been used to distinguish and select for chemical analysis the various platinum- and palladium-bearing minerals present in concentrates of Bushveld platinum ore. The name cooperite is retained for PtS, tetragonal space-group D^9_{4h}. The face-centred unit cell with edges $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å., contains 4PtS. The structure is a simple type of fourfold co-ordination built up from planar PtS_4 groups and tetrahedral Spt_4 groups, the Pt–S distance being 2·32 Å. Laurite (RuS_2) occurs as small pyritohedral-cubic crystals and has the pyrite structure with unit-cell edge $a = 5{\cdot}59$ Å., and parameter u between 0·39 and 0·395. The third mineral (Pt,Pd,Ni)S containing about 20 % Pd and 5 % Ni, is also tetragonal with unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å. The unit cell contains 8(Pt,Pd,Ni)S, and the space-group is D^2_{4h}. The name braggite is proposed for this mineral as being the first new mineral to be discovered by X-ray methods.

Appendix.—Notes on the analyses, and on the synthesis of the sulphides of the platinum group. (By M. H. Hey.)

For those minerals in the Transvaal platinum concentrates which are insoluble in aqua regia, fusion methods are very unsatisfactory when small quantities have to be dealt with, as the amount of flux has generally to be quite disproportionate to the amount of material. It was found best to heat the minerals in a current of air, in a small silica-glass tube slipped into a wider one of the same material; the latter was bent and drawn down to a jet at the exit end, and the

sulphur oxides collected in ammoniacal hydrogen peroxide, and weighed as barium sulphate. Some difficulty was experienced in obtaining total absorption of the sulphur, as it is oxidized to sulphur trioxide, fumes of which can be seen in the tube, and this tends to give a troublesome fog (the oxidation to the trioxide is, of course, due to the catalytic action of the platinum metals).

The advantage of this process for the present purpose lay in the metal remaining as a bead instead of subliming as chloride, as it does if chlorine is used to attack the mineral; and an X-ray photograph of the metal bead may afford useful information. Cooperite and braggite leave beads of pure metal, readily soluble in aqua regia, but the laurite left a residue containing 9 % oxygen, due to superficial oxidation, and gave an X-ray photograph agreeing with RuO_2. This oxidized bead was reduced in hydrogen, to get the weight of the metal, and then heated in a current of chlorine to bring it into a soluble form for identification tests.

The small amount of material available limited the analyses to the principal constituents, and it was impossible to test accurately for the presence of osmium, iridium, ruthenium, or rhodium in the cooperite and braggite; but it could be shown that the laurite contained no appreciable amount of platinum, palladium, or iridium.

An accurate micro-balance was not available, but the analyses were carried out on a good analytical balance with the help of a reading microscope to follow the swing of the pointer. The weighings were probably accurate to about $\pm 0{\cdot}02$ mg., and the weight of material used for each analysis of the minerals is given in tables I–III. The synthetic products were available in larger quantity (0·2–0·4 gm.) and their analysis presented no difficulties.

The synthesis of the platinum sulphides was undertaken at a time when accurate analyses of any of the minerals seemed impossible owing to the minute amount of material available, and confirms the conclusion of W. Biltz and R. Juza[1] that PtS and PtS_2 are the only sulphides formed, processes supposed to give Pt_2S_3 or Pt_5S_6 leading to mixtures of mono- and disulphide. Biltz and Juza's work shows that the sulphide to be expected depends simply on the temperature and sulphur vapour-pressure, hence there seems no point in giving full details of all the processes tried.[2] But it may be noted that the

[1] W. Biltz and R. Juza, Zeits. Anorg. Chem., 1930, vol. 190, p. 161.

[2] The methods used were those of L. N. Vauquelin, Schweigg. Journ., 1817,

sodium and potassium platinum sulphides described by R. Schneider were not obtained, and the possibility of their existence requires re-investigation.

The syntheses of palladium sulphides were made mainly on the chance of one of them proving allied to one of the two rare, unidentified minerals in the Rustenberg concentrates, and it was surprising to find that PdS gives a powder photograph almost identical with that of braggite, which contains about 60 % platinum. So far as they go, the experiments show that PdS is the most stable of the palladium sulphides.[1] The stable existence of PdS_2 is doubtful, R. Schneider's process giving a mixture of PdS and sulphur. The reported insolubility of Pd_2S in aqua regia (both PdS and palladium are readily soluble) makes it probable that it can exist, but it was not obtained, and the exact conditions under which it is stable require investigation.

Laurite has been synthesized by H. Deville and H. Debray,[2] though the identity of the synthetic and natural product was not too firmly established. Indeed, Mr. Bannister's X-ray study of Borneo laurite forms the first satisfactory proof that the mineral is RuS_2, as Dana, L. J. Spencer and others believe [3], rather than Ru_2S_3, as it is given by H. E. Roscoe and C. Schorlemmer, and by A. J. Webb.[4]

vol. 20, p. 394; R. Böttger, Journ. Prakt. Chem., 1834, ser. 1, vol. 3, p. 267; R. Schneider, Journ. Prakt. Chem., 1873, ser. 3, vol. 7, p. 224; H. Deville and H. Debray, Compt. Rend. Acad. Sci. Paris, 1879, vol. 89, p. 587; and W. Knop, Chem. Centr., 1859, p. 18.

[1] The methods used were those of F. Roessler, Zeits. Anorg. Chem., 1895, vol. 9, p. 31; R. Schneider, Ann. Phys. Chem. (Poggendorff), 1870, vol. 141, p. 519; L. N. Vauquelin, Ann. Chem. Phys., 1813, vol. 88, p. 190; and Smith and Keller, Ber. Deut. Chem. Gesell., 1890, vol. 23, p. 3373.

[2] H. Deville and H. Debray, Compt. Rend. Acad. Sci. Paris, 1879, vol. 89, p. 587.

[3] Dana Syst. Min., 6th edit., 1892, p. 93; L. J. Spencer in Sir Edward Thorpe's Dictionary of Applied Chemistry, 2nd edit. (London), 1924, vol. 4, p. 38; W. F. de Jong and A. Hoog, Rec. Trav. Chim. Pays-Bas, 1927, vol. 46, p. 173.

[4] H. E. Roscoe and C. Schorlemmer, Treatise on Chem., 4th edit. (London), 1907, vol. 2, p. 1291; A. J. Webb, in Sir Edward Thorpe's Dictionary of Applied Chemistry, 2nd edit. (London), 1924, vol. 5, p. 721.

Explanation of Plates VII and VIII.

X-ray photographs of minerals from Transvaal platinum concentrates. All these photographs were taken with filtered copper radiation $\lambda = 1{\cdot}539$ Å., and with the same cylindrical camera, diameter 6·04 cm. A length of 15 cm. on all the original films is equivalent to 10 cm. on the reproduced figures.

Fig. 3. Rotation photograph of cooperite crystal no. 2 about the axis [100].

Fig. 4. Rotation photograph of a laurite crystal about a cube axis.

Fig. 5. Powder photograph of ruthenium dioxide.

Fig. 6. Powder photograph of ruthenium.

Fig. 7. Powder photograph of synthetic PtS.

Fig. 8. Rotation photograph of a crystal fragment in random orientation for identification. This photograph is completely superposable upon the powder photograph, fig. 7; the mineral fragment is therefore cooperite.

Fig. 9. Rotation photograph of a crystal of braggite about the axis [001].

Fig. 10. Powder photograph of braggite.

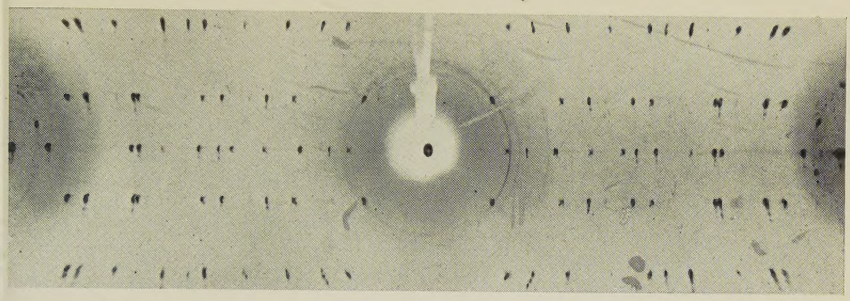


Fig. 3.

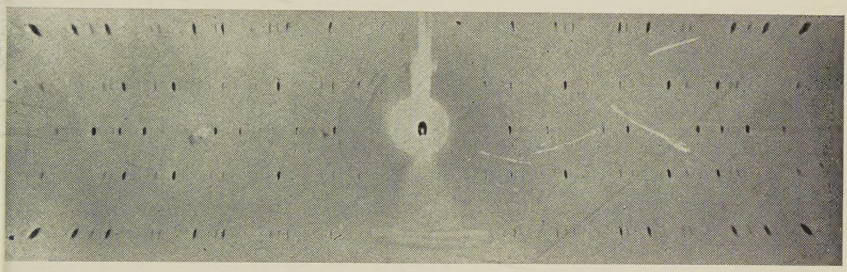
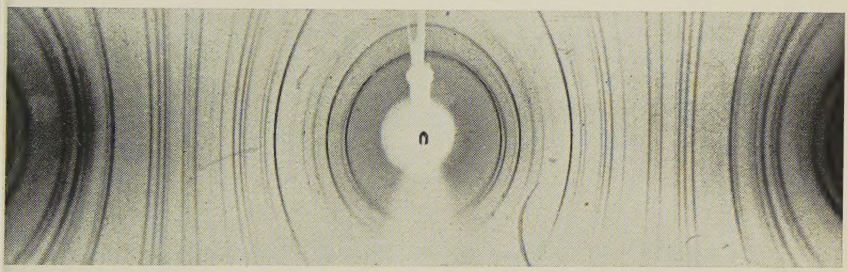


Fig. 4.



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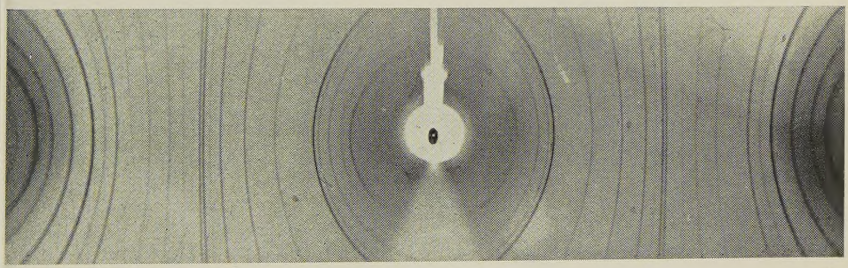

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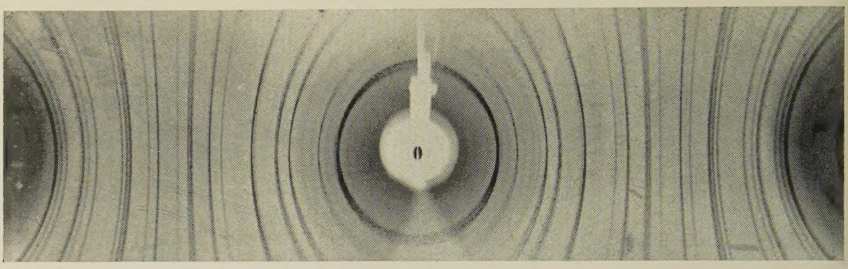

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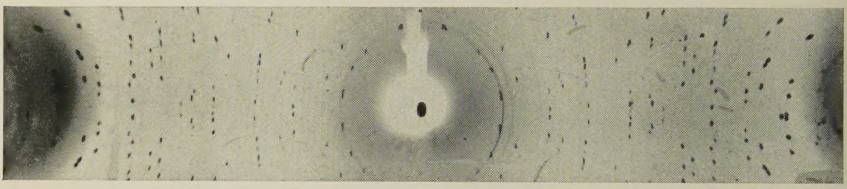

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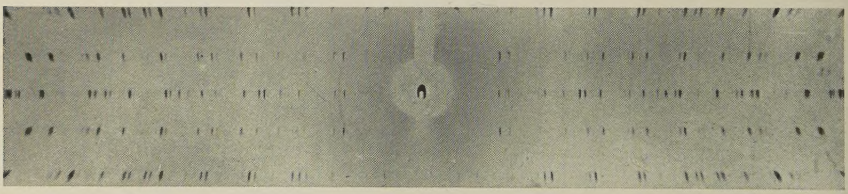

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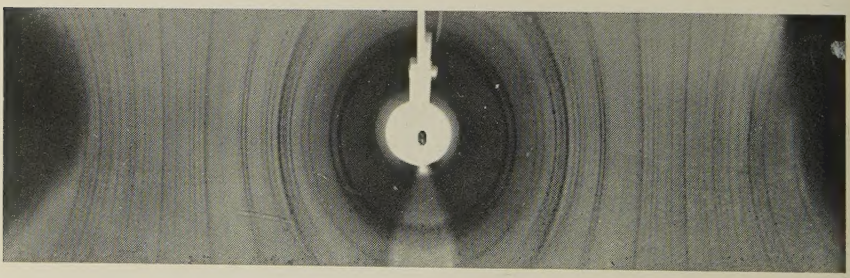

Fig. 10.